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Fall Glass Division Meeting

Bedford Springs Hotel BEDFORD, PENNSYLVANIA, OCTOBER 12-14, 1960

● THE FALL GLASS DIVISION MEETING of the American Ceramic Society was held at the Bedford Springs Hotel, Bedford, Pennsylvania. Approximately 400 were registered, including 79 women. Several foreign glass technologists were present, including Emil W. Deeg and Carsten Eden of the Jenaer Glaswerk; Shoichiro Nagia, Nihon University, Japan; and Shoji Tsuchihashi, also from Japan, who is presently at Stanford Research Institute. The Program was planned by Clarence L. Babcock, Owens-Illinois Technical Center; Harold E. Simpson, College of Ceramics at Alfred University; and Charles L. McKinnis, Owens-Corning Fiberglas Corporation. There were 17 papers plus a workshop on "Methods of Studying Crystallization Phenomena in Glass."

For the Ladies

The ladies' program, which was concluded with a lecture on flower arrangements, was planned by Mrs. Charles E. Gum, General Chairman; Mrs. Frederic L. Bishop, Registration; Mrs. C. L. Cruikshank, Square Dance; Mrs. James P. Pool, Ladies' Golf; Mrs. Philip Sauereisen, Bridge and Canasta; Mrs. J. C. Keaney, Jr., Ladies' Prizes; Mrs. Frank R. Bacon, Brunch; Mrs. D. Owen Evans; Mrs. Seth G. Merriman; Mrs. Thomas B. Montgomery; Mrs. Guy E. Rindone; Mrs. Dudley C. Smith; Mrs. Howard R. Swift; Mrs. Ralph L. Weaton; and Mrs. Bradley E. Wiens.

Spring Meeting of the American Ceramic Society will be held at the Royal York Hotel, Toronto, Ontario, Canada, on April 23-26, 1961

Papers

THURSDAY MORNING

Chairman: GUY E. RINDONE

Pennsylvania State University, University Park, Pa.

The Thermal History of Glass I. The Density Variations of Glass During Crystallization and Heat Treatment

By *Bernard L. Steierman* and *Tryggve Baak*, Fundamental Research Sec., General Research Div., Owens-Illinois Technical Center, Toledo, Ohio.

Dr. Steierman, who presented the paper, pointed out that crystallization of glass is not ideal in the classical thermodynamic sense. Irreversible thermodynamics or kinetic view points must be used. The kinetic approach was adopted with density change as a measured parameter. Glasses high in SiO_2 and Al_2O_3 with minor amounts of MgO, Li_2O, and TiO_2 were used. These glasses were heat treated at 700, 800, 900, and 1000°C. at various time intervals ranging from ½ to 4 hours. The density was determined by the pycnometer method. Density data was converted to fraction of volume crystallized by using specific volumes of glass, crystals, and test sample:

$$x_c = \frac{V_g - V_t}{V_g - V_c}$$

Where V = specific volume, g = glass, t = sample, and c is the final sample. When x_c was plotted against log time (Log t), the straight line region of plot at 800 — 1000°C. was given as evidence of concurrent nucleation and crystal growth. This was further demonstrated by electron micrographs. "Knee" of curves at short time intervals suggested a low temperature process, but

X-ray and electron micrograph evidence did not confirm this condition.

The high temperature "shoulder" of the curve gave evidence of transformation, and this was confirmed by X-ray data.

The density method was believed to be useful even in complex systems, but its use in conjunction with other techniques is recommended.

Crystals in Glass and Their Significant Effect on Physical Properties

By *Francis C. Lin*, Westinghouse Electric Corp., Ceramics Section, Pittsburgh 8, Pa.

The author described his studies of nucleation and crystal growth phenomena by means of the electron microscope. Crystal formation in glass by induced nucleation and the concept of nucleation and growth of crystals were also discussed. It was pointed out that crystals can be formed only if there is homogeneous nucleation within the glass matrix. Hetrogeneous nucleation on the surface of the melt will result in devitrification.

It was suggested that the induced nucleation and crystal formation in glass may serve as a means to study more complex glass structures. With modern techniques such as an electromicroprobe, electromicroscope, and X-ray diffraction, the crystalline structure can be correlated with the observed physical properties.

Experimental results were reported on the effects of crystallization on physical properties of Al_2O_3-5MgO.-8SiO_2 glass system. These properties included: deformation temperature, linear thermal expansion, dielectric strength, electrical resistivity, density variation during heat treatment and Te-value as function of crystallization. The properties were then correlated with crystal structure from X-ray diffraction data.

Diffusion of Oxygen from Contracting Bubbles in Molten Glass

By *R. H. Doremus*, General Electric Laboratory, Schenectady, N. Y.

Some experimental measurements on the rate of contraction of oxygen bubbles in molten glass were compared to an equation for the diffusion-controlled contraction of a sphere. This comparison indicated that the equation was valid until about 80 per cent of the oxygen had been diffused from the bubbles so that the diffusion coefficient of the oxygen in the molten glass could be calculated from the experimental measurements. These values of the diffusion coefficient were higher than would be expected from the Stokes-Einstein equation for diffusion in liquids. Thus, it was concluded that some short circuiting mechanism such as diffusion in glass channels was operative. It also appeared that the oxygen was diffused in the glass as atoms, rather than as molecules. From contraction measurements on glasses with different fining agents it was concluded that the mechanism of fining by such agents as antimony and arsenic oxides is not the discharge of oxygen gas as has been generally supposed, but is rather the reduction of the concentration of oxygen in the glass, causing the oxygen in the bubbles to be diffused into the glass more rapidly.

Ion Exchange Between Soda-Lime Glass and Molten Lithium and Silver Salts

By *C. M. Hollabaugh* and *F. M. Ernsberger*, Pittsburgh Plate Glass Co., Glass Research Center, Pittsburgh 38, Pa. Presented by Mr. Hollabaugh.

A method was described for determining the concentration profile of alkali ions near the surface of glass. This method was employed to determine diffusion constants for lithium and silver ions diffusing into glass from a molten salt bath. The results of these experiments indicated that the rates of exchange between the lithium ions and the sodium ions in the glass depend not on the mobility of lithium ions as previously assumed by LeClerc, but on the mobility of the sodium ions which are being diffused out of the glass.

WORKSHOP

The Thursday afternoon session was devoted to a Workshop on "Methods of Studying Crystallization Phenomena in Glass." Chairman: H. R. Swift, Libbey-Owens-Ford Glass Company, Toledo, Ohio.

Method for Studying the Devitrification Process in Glass

By *R. J. Jaccodine*, Bell Telephone Laboratories, Allentown, Pa.

Although devitrification studies are generally made by optical examination of the more opaque clusters of crystals that form in the transparent glass matrix, some electron microscopic studies have also been undertaken by replica techniques. An etching technique was described which allows a study of the devitrification process when neither of the techniques described above are adequate. This inadequacy was particularly evident in the early stages of the growth process when opaque crystals are not descernible. The etchant served to differentiate the crystal phase from the matrix material.

Through the use of this technique, the size of crystals was observed at 3 different devitrification temperatures as a function of time using 30 per cent Li_2O-SiO_2 glass. From the size versus time curve, information was obtained concerning the growth rate and the kinetics of the crystallization process.

The etch was used on vitreous material where a range of etching structures has been observed. Some examples of these structures were shown.

It was believed that glass undergoes a nucleation and growth of crystals when subjected to heat treatment. This process is not unlike similar processes in other solid solutions. The resulting structures cause a distinct and sometimes drastic change in the properties of the glass. This crystallization process is of fundamental interest and bears on the problem of the nature of glasses.

A Hot-Stage Petrographic Microscope for Glass Research

By *T. W. Brock,* Owens-Illinois Technical Center, Toledo, Ohio

Construction details of a petrographic microscope modified for high temperature investigations were described and operational features and sample preparation procedures discussed.

The equipment has an optical system providing a magnification of 70X with means for recording the results photographically. The temperature range is 300-2000°F.

Typical photographs of crystals developed in glass at elevated temperatures were shown along with a crystal growth rate curve of crystalline phases.

Determination of Per Cent Crystallinity of Partially Devitrified Glass by X-ray Diffraction

By *Stanley M. Ohlberg* and *Donald W. Strickler,* Pittsburgh Plate Glass Co., Pittsburgh, Pa. Presented by Mr. Ohlberg.

An X-ray diffractometer technique similar to one used to determine the crystallinity of elastomers was applied to partially devitrified glass. The amorphous fraction, f_a, of partially devitrified glass was determined by comparing the noncrystalline intensity of a radial section with that of the glass prior to devitrification. The crystalline fraction was then found by difference, $f_c = 1 - f_a$. The experimental technique was described, the limitations and assumptions discussed, and some results on synthetic mixtures presented. This method was found to be rapid, virtually independent of the crystalline species present, and accurate to ± 5 per cent or better.

Methods Used for Studying Glass Devitrification Phenomena at the Bureau of Standards

By *Given W. Cleek,* National Bureau of Standards, Washington, D. C.

The temperature range in which devitrification can occur is of considerable interest to the glass technologist in the development of new optical glasses. The procedure described in this paper was to make melts of the experimental glasses in series, varying one component at the expense of another, and determining the liquidus temperature for each glass. Through the use of compositions at or near the minima of the liquidus curves, stable multi-component glasses of new compositions were developed.

The apparatus used for these determinations is that described by Grauer and Hamilton in their paper, "*An Improved Apparatus for the Determination of Liquidus Temperatures and Rates of Crystal Growth in Glasses,*" J. Res. NBS *44* 495 (1950) RP 2096.

This method of determining liquidus temperatures is simple and rather versatile. It has been used on many different types of glass having widely varying compositions and devitrification characteristics. Its use allows the glass technologist to assess quickly the effects of composition changes on the liquidus temperatures of experimental glasses and obtain a general idea of the ease of devitrification of each glass. The method has also proved useful in the study of liquid immiscibility in systems where the normal quenching techniques did not give satisfactory results.

Liquidus Measurement Methods Used for Control Purposes

By *Leon R. Scholtzhauer,* Corning Glass Works, Corning, N. Y.

The author pointed out that a practical method of liquidus measurement contributes information which is directly valuable to glass melting and glass delivery processes. Certainly, determination of liquidus temperature is helpful for establishing minimum operating temperatures. These determinations also assist a program of new glass composition development.

A method which satisfactorily meets these requirements is essentially the Silverman method, first described in 1939. The apparatus and procedure used by Corning Glass Works was described briefly.

Immediately prior to each liquidus run, the gradient furnace was probed with a movable platinum-platinum-10-per-cent-rhodium thermocouple enclosed, except for the junction, in double-bore tubing. Temperature measurements along the length of the core were made in regular increments from a reference point mounted on the front face of the furnace. These values were plotted for later use in the determination. The glass-filled boat was then carefully positioned in the desired portion of the gradient, using this same reference point.

Upon removing the sample from the furnace (care being taken not to tip or incline the boat in this process), it was allowed to cool in air to room temperature. The boat was carefully marked at 1-inch intervals to maintain accurate record of distance along the length of the boat. The surface of the glass was examined with a stereomicroscope to determine the point at which surface devitrification terminated. The distance from the furnace reference point was measured, and the surface liquidus temperature was then obtained by referring to the thermal gradient plot determined at the start of the run.

Inasmuch as the glass fractures upon cooling in a refractory boat, it was necessary to impregnate the glass contents with glycol phthalate, a thermoplastic resin, before sawing and thin sectioning. Where thin-walled platinum boats are used, it is not necessary to impregnate since fracturing is at a minimum. After marking reference distances on the glass surface, the platinum was quite easily stripped from the glass specimen. The appropriate portion could then be thin-sectioned directly.

Thin sections were examined with the aid of a polarizing microscope; first, to determine the liquidus point for each crystalline phase; and secondly, to identify each phase. Upon determining the position of the liquidus point in terms of distance from the furnace reference point, the actual liquidus temperature may again be read

directly from the temperature gradient plot determined at the start of the run. The internal liquidus should be marked midway between the glass surface and the bottom of the boat. Marking in this standard manner reduced errors which might have been introduced by volatilization and refractory corrosion effects.

The remaining portion of the liquidus boat can be used to provide additional samples for study. Often it is desirable to work with crushed fragments under the microscope or to obtain X-ray identification of a crystalline phase. Adequate sample for this work may be taken from the colder, unsectioned portion of the boat. Also, where surface devitrification occurs at a temperature substantially higher than the internal liquidus temperature, it may be desirable to prepare another section from the hotter end of the boat for petrographic study.

A major advantage of the described method accrues from the fact that professional skill is required only for the microscopic step of the procedure. Technicians are able to carry out the mechanics and maintain records and equipment. Also, each determination results in a thin section that can be filed for ready reference.

Accuracy, while dependent upon technique and furnace control equipment, has been found very adequate for the majority of industrial appplications. Accuracy of the method can be maintained easily within ± 4°C, depending upon the size of the gradient used.

Devitrification Studies on Borosilicate Glasses

By *C. L. McKinnis*, Owens-Corning Fiberglas Corp., Granville, Ohio

All commercial glass manufacturing processes require that the molten glass be conditioned near to the upper temperature limit of the devitrification range and/or pass through the temperature range conducive to devitrification, prior to fabrication. The presence of crystalline material, either of embryonic or finite dimension is detrimental not only to the continuity of the glass fabrication process, but also to the properties of the produced vitreous material as well. A consideration of the deleterious effects of devitrification prompted a new experimental approach to devitrification measurements and procedures which depart somewhat from the more classical methods. This new experimental concept allows for *(1)* a continuous determination of the temperature before, during and at the completion of the experimental run, and *(2)* a close duplication of the heat cycle experienced in actual production operations.

The sample holder, a platinum devitrification tray similar in design to that developed and utilized at the National Bureau of Standards, contains two rows of 55 perforated cells each. Glass chips, of approximately 0.1 inch in diameter are placed into each cell and the prepared tray given a predetermined heat treatment. The effects of the devitrification produced by the heat treatment are determined by direct microscopic observation, generally, without further preparation.

Either of two temperature controlled, platinum wound, horizontal tube furnaces are used for heat treatment, one having a temperature gradient, the other a constant temperature. Each furnace has twelve continuous recording thermocouples (on one-inch centers) which protrude into the actual heat treating zone. This allows for continuous determination of the temperature before, during and at the completion of an experimental run.

With both a temperature gradient and a constant temperature available, a wide variety of heat treating cycles may be used. For example, the glass may be *(1)* first equilibrated at some temperature in excess of the liquidus temperature (constant temperature) and then while still hot placed into the range of temperatures conducive to devitrification (temperature gradient), or *(2)* heated from room temperature up through the devitrification range (instant or gradient temperature). In addition, the dissolution of previously crystallized glass may likewise be determined (constant temperature). In all cases, the temperatures may be ascertained as a function of time.

Heat treating times may range anywhere from minutes to hours, depending upon the ultimate utilization of the data; shorter times are used when it is desired to approximate the heat cycle of a particular manufacturing process, longer times when equilibrium results are required.

The design of the equipment and its utilization were discussed, along with the results of actual experimental determinations.

FRIDAY MORNING

Chairman: CLARENCE L. BABCOCK
Owens-Illinois Technical Center, Toledo, Ohio

Kinetics of Reactions Occurring in the Glass Preparation Process

By *Elwin L. Johnson*, Materials Research Dept., Central Research Laboratories, Texas Instruments Inc., Dallas, Texas, and *F. V. Tooley*, Department of Ceramic Engr., University of Illinois, Urbana, Ill. Presented by Mr. Johnson.

The progress of reactions occurring in the process of glass preparation was followed by thermogravimetric analysis and quantitative X-ray diffraction analysis. Three soda-lime-silica compositions and 1 soda-silica composition were studied.

The rate-controlling process was found to be that of the silica lattice breakdown in the soda-lime-silica compositions, in the sodium metasilica compositions, and in the sodium metasilicate solution process in the soda-lime composition.

The sequence of reactions was given for the Na_2CO_3-$CaCO_3$-SiO_2 and Na_2CO_3-SiO_2 systems at temperatures above the liquidus of the oxide compositions.

Activation energies were presented for the decomposition of calcium carbonate in a soda-lime-silica glass batch and for the reaction between sodium carbonate and silica in the soda-silica glass batch.

Correlation of Strength of Glass with Fracture Flaws of Measured Size

By *Errol B. Shand,* Technical Consultant, 155 Reynolds Ave., Corning, N. Y.

Studies of strength of glass and its mechanism of fracture have been hampered seriously because of the very small amount of accurate information now available regarding the actual dimensions of the flaws which initiate failure. The purpose of this paper was to develop a means whereby correlations could be established between dimensions of these flaws and breaking stress as a function of time. A single small flaw was produced in the glass surface by pressing a wedge-shaped tungsten-carbide tip against the glass. Dimensions of this flaw or crack were measured after the glass was fractured from boundary markings observed on the mirror surface of the fracture. A polarizing microscope was used for this purpose. Considerable difficulty was experienced in producing cracks of consistent properties and in interpreting and measuring markings on the mirror surface. Cracks were cleaved under the microscope while the depth was measured. After fracture, these identical flaws were again measured so that a surer interpretation could be effected. It was found that the presence of residual stresses in the glass had a considerable influence on flaw formation and that breaking stresses were increased by surface compression to an extent considerably more than is predicted by elementary theories of tempering effects.

In carrying out fracture tests on these cleaved specimens the data from each specimen represented a complete point on the stress-time curve. Although all fracture cracks will not be of the same depth, adjustments can be made to bring all data to the same depth basis. Flexure tests were carried out on glasses of several compositions. The one-second breaking stresses of these glasses, considering a semicircular fracture crack 0.002 inch deep, were as follows: lead-alkali glass, 6800 p.s.i.; soda-lime glass, 9000 p.s.i.; 96 per cent silica glass, 11000-12000 p.s.i.; borosilicate low expansion, 12000 p.s.i.; and aluminosilicate glass. 13800 p.s.i. From these data and also the elastic moduli, the fracture energies per unit area of surface opened can also be computed for these same conditions. The values were found to range from 1160 ergs/cm^2 for the lead-alkali glass to 3480 ergs/cm^2 for the borosilicate glass. These values are much in excess of corresponding surface energies as commonly measured.

On some basis the breaking stresses will correspond to the relative intrinsic strengths of the glasses. It was concluded that the intrinsic strength of the aluminosilicate glass is double that of the lead-silicate glass.

While these tests were of a preliminary nature and were made to find out whether material differences actually exist between glasses of different compositions, it is believed that the more intensive application of these methods can increase our understanding of fracture phenomena in glass and in other brittle materials.

A New Method for the Experimental Determination of the Limiting Molecular Strength of Glass

By *F. M. Ernsberger* and *D. E. Braithwaite,* Glass Research Center, Pittsburgh Plate Glass Co., Pittsburgh 38, Pa. Presented by Mr. Ernsberger.

Direct experimental determination of the limiting molecular strength of glass is ordinarily frustrated by the existence of flaws in the surface of the specimens. The influence of surface flaws can be reduced to a large extent by careful preparation and handling of the specimens, but there is no way to determine whether surface flaws have been entirely eliminated in such experiments.

The paper described an alternative experimental approach which avoids these difficulties and is based on the concept of converting the surface of the specimen to the liquid state. In this condition all pre-existing flaws were healed, and no new flaws were formed. The conversion was accomplished by heating the specimen rod in contact with sodium vapor at about 400°C until the surface was liquefied to a suitable depth. The treated specimen was then broken in simple tension.

Some Glasses for the Transmission of Ultraviolet Radiation

By *Francis W. Glaze, Jack M. Florence, Jerome S. Osmalov, Douglas H. Blackburn, Herman F. Shermer,* and *Mason H. Black,* National Bureau of Standards, Washington 25, D. C. Presented by Mr. Glaze.

The ultraviolet transmission and other properties of a series of Li_2O-BeO-(SiO_2 + B_2O_3) glasses, melted in platinum, were reported. The highest transmittance for a thickness of 1 mm. was 13.0 per cent at the wavelength of 253.5 mu. Melting in porcelain crucibles with a reducing agent to improve the transmission was unsuccessful because of the corrosive nature of the glass. Such a glass had no transmittance below 330 mu.

The properties of a series of metaphosphate glasses were also reported. Porcelain crucibles lined with ZrO_2 and fired at 1500°C were found suitable for melting these glasses. A glass with the composition of $Mg(PO_3)_2.NaPO_3$ had a transmittance of 79.5 per cent at 253.5 mu for a thickness of 1 mm. The reduction of Fe^{3+} to Fe^{2+} greatly increased the ultraviolet transmission of these glasses.

Besides ultraviolet transmission measurements, linear cofficient of expansion, elastic moduli, density, and index of refraction were determined on a number of the glasses. Also, those samples still available after approximately 8 years were examined for surface deterioration.

Solutions for Unsteady State Heat Flow in Situations Representing Some Types of Glass Molding

By *A. F. Cooper, Jr.,* Ceramics Div., Dept. of Metallurgy, Massachusetts Institute of Technology, Cambridge, Mass.

Calculated temperature distributions were presented for one-dimensional heat flow between slabs initially at different uniform temperatures in instances when *(a)*

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FIG. 1. Various types of ampules manufactured in the new Wheaton Glass Company plant, Millville, N.J. They are produced from Type 1 borosilicate glass and are used for injectibles.

FIG. 2. Stretching from one end of the plant to the other are nineteen automatic gas-fired lehrs for annealing ampules and vials. Each leh has shown a 25% increased yield of quality containers.

Radiant Heating Speeds Ampule Production

by George J. Straubmuller, Vice President, Tubing and Tubing Products Division, Wheaton Glass Company, Millville, New Jersey

Wheaton Glass Company, oldest producer of tube-made ampules and vials in the United States, added a new plant to its manufacturing facilities in Millville, N.J., last year. Production is devoted to high-quality glass ampules for injectibles (Fig. 1), and vials for injectibles, capsules, tablets and cosmetics.
This article describes the latest glass-making techniques and advanced heat-processing equipment which helped increase the company's production rate and reduce its manufacturing costs.

ED.

● EQUIPPED WITH RADIANT-BURNER ROOF PANELS, nineteen compact automatic lehrs at Wheaton Glass Company's new Millville, N.J., plant have increased the production rate for annealing ampules and vials by 25 per cent, compared with the previous flame-burner method. A 45-foot-long lehr using the radiant-heating method has doubled the production rate over the former flame-heated method for fusing printing into ampules.

To coordinate the new plant's automatic glass-making techniques with this advanced heating method, Wheaton Research and engineering staffs worked closely with engineers of Selas Corporation of America. With the modernized, better synchronized production system, many other benefits are also being gained.

The tubing, from which ampules and vials are made, is weighed with microscopic accuracy to segregate variations in the wall thickness of the glass. To eliminate the need for constant changing and adjusting of heat in any one lehr, the various thicknesses are grouped to run individually through different forming machines and annealing lehrs.

The 5 foot lengths of tubing are taken to the work area and fed into a line of 25 ampule and vial forming machines. The ampule stems are pulled, constriction formed and workpieces are bottomed. Released from the forming machines and automatically transferred onto conveyors, the glass pieces have their stems trimmed and glazed, constriction scored, gold band identifications applied and stem O.D. gaged.

Completely formed and marked, the ampules, or vials, are automatically fed onto the wire mesh conveyor belt behind each forming machine, and carried to and through the adjoining lehr for the critical annealing operation (Fig. 3).

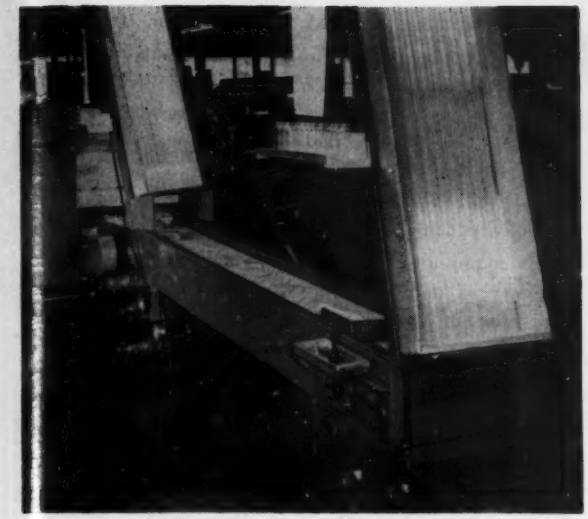

FIG. 3. Vials conveyed into lehr for the critical annealing operation. Two stacks of tubing are kept in a convenient place over conveyor, to be fed into forming machine at right (not visible).

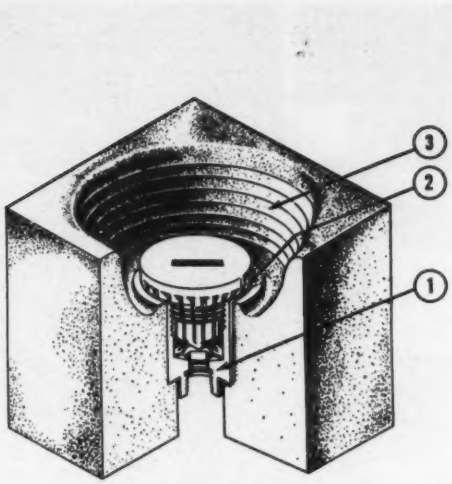

FIG. 4. Radiant burner diagram. Gas-air mixture enters tube (1); moves to burner tip and passes through threaded refractory orifices (2); burns radially on specially grooved and contoured refractory cup surface (3).

Lehr Operation

A few seconds after the glass pieces enter the lehr, they are exposed to heat from the radiant-burner roof panel, which is located 1½ feet inside the entrance and 1½ feet above the ware. The temperature curve in the heating section of each lehr is adjusted according to the thickness of the glass being treated, as mentioned above. Peak temperatures range between 1200° and 1240°F. Traveling in such close proximity to the heat source, ampules and vials require only 3 minutes' exposure to the burners to bring them to their desired temperature.

During this critical 3 minute travel under the burners, extremely close control of heat input to the glass pieces is a "must." The different work-piece temperatures—to which each of the burners in the ampule lehr roof panels and each of the burners in the vial lehr roof panels are adjusted—must be held to within ± 5°F of the predetermined levels. The planned temperature curve rises from low to a peak at the mid-point of the roof panel and then tapers off gradually, and must be followed with the utmost precision.

If the temperature exceeds its predetermined peak level by more than 5°F, or does not taper off as planned,

FIGS. 5, 5a. Operators inspect vials (left) and ampules (right) for imperfections and gage correctness; then package them. Unsatisfactory containers are conveyed to a "reject" chute (foreground). Vial lehr requires two operators and a slightly wider conveyor belt.

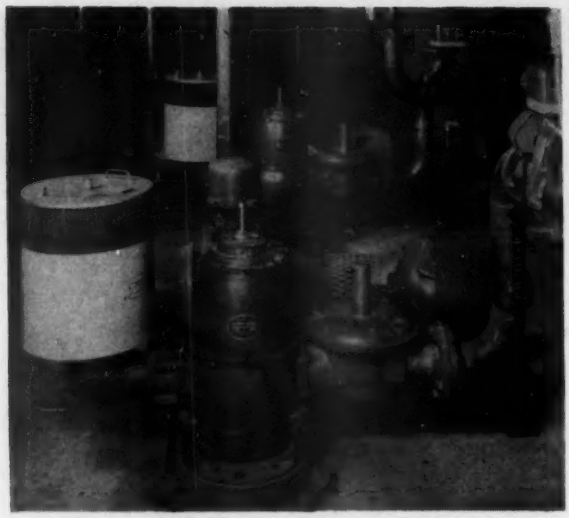

FIG. 6. In separate room two combustion controllers alternately supply fuel to 20 lehrs. Natural gas from low-pressure plant line and air drawn from room are mixed in precise ratio, then compressed to several pounds pressure for delivery to burners.

the delicate glass pieces can be misshapen. Should temperatures not reach predetermined levels, the strain would not be completely eliminated from the glass, and the ampules and vials would not meet the rigid polariscope tests that follow.

The previous method of annealing ampules and vials, with flame burners, did not provide the necessary temperature control and uniformity. As a result, hot and cold spots often developed. Considerable production time was lost on re-runs and rejects were high. With the precision method now in effect close control and uniformity of heating has been assured.

Radiant Heating Method

The radiant heat from the burners is created by burning closely-controlled gas-air mixtures against specially grooved and contoured, cup-shaped refractory surfaces (Fig. 4). The surfaces become incandescent and beam radiant heat uniformly to the ampules and vials, without harmful hot-spot flame impingement. Combustion is completed entirely within the cup.

This combination of a high thermal head and a close proximity of the heat source to the glass ware makes faster annealing cycles possible, and eliminates re-runs as well as costly rejects.

Accuracy of temperature control in the heating system is further assured through the maximum combustion efficiency provided by two combustion controllers (Fig 6), used alternately to supply the entire line of lehrs with fuel. The combustion controller, heart of the combustion system, takes natural gas from the low pressure plant line, draws air from the room, mixes the two in precise ratio, and compresses the mixture to several pounds pressure for delivery to the burners.

After 3 minutes' exposure to this accurately controlled heat, the glass workpieces enter the controlled-cooling zone. Passage through this zone, where temperatures of the glass pieces are brought down gradually to a safe level for exposure to room air, takes only 7 minutes—a total of 10 minutes in the lehr for each glass piece.

As workpieces emerge from the ends of the ampule and vial lehrs, operators inspect them for imperfections and gauge correctness (Figures 5 and 5a). A second and more rigid inspection, including examination under a polariscope, is given by quality control experts. In Figure 6 the operators placed a workpiece over the

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FIG. 7. Heating section of lehr for fusing silk screen printing into glass. Radiant burners, with pressure gage connected to each one for individual control, are patterned along sides of lehr. Instrument panel board (extreme left) controls all steps in printing and heating operations.

FIG. 8. After three minutes' controlled heating and cooling, ampules emerge from 46-ft. lehr where silk screen printing is fused into glass.

Conditions of Glass Formations Among Simple Compounds* Part III

IN FOUR PARTS

by W. A. Weyl and E. C. Marboe, College of Mineral Industries, The Pennsylvania University, University Park, Pennsylvania, U.S.A.

Or Variations of Glass Compositions and the Enforcement of Glass Formation

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I. INTRODUCTION

Statement of the Problems

● The problem discussed in the preceding papers[1,2] namely, the conditions which a simple inorganic substance has to meet in order to be able to form a glass is one of fundamental importance for the physical chemistry of the solid state. From the viewpoint of a glass technologist, however, very few simple compounds are used in their vitreous state. Silica itself and to a lesser extent arsenic trisulfide are the only glasses of technical interest which a chemist would call simple compounds. The bulk of technical glasses has a more complex and in most cases a non-stoichiometric composition. We have seen, however, that even a so-called simple glass may actually represent a complex system from a physicochemical point of view. This is one of the reasons why glasses which are, chemically speaking, one component glasses, e.g., vitreous B_2O_3, resemble in their melting and nucleation behavior glasses of complex compositions.

Chemical complexity of technical glasses offers the possibility of obtaining a desirable combination of properties and a low liquidus temperature.

Silica is the prototype of a glass-forming oxide. The manufacture of this glass, however, is difficult because of the high temperatures which are required. This might suggest to a scientist the idea to modify a silica glass and to improve its meltability. However, a scientist undertaking this task might well be discouraged and give up after many unsuccessful experiments. He may start out with systematic additions of 1, 2, 4 and 8 per cent Na_2O to silica and be disappointed because his experiments reveal that even the smallest additions of alkali cause the silica to lose its ability to form a glass. He obtains only products which are essentially cristobalite embedded in a glassy matrix. Hence he turns to similar experiments adding MgO or CaO to quartz, but his products of fusion bear even less resemblance to glass. Other oxides such as Al_2O_3, ZrO_2, or TiO_2 give equally negative results. Only if the discouraged scientist turns to a very unorthodox method and prepares random mixtures which contain much more alkali than 8 per cent or combinations of alkali with CaO, Al_2O_3, etc. will he discover composition regions in which stable and useful glasses can be obtained.

Some binary systems containing silica as one component show such rapid nucleation of cristobalite that they are useless as glasses and others show immiscibility even in the liquid state. There are very few oxides which are compatible with SiO_2 and, indeed, among water insoluble products the lead silicate glasses which are used for X-ray protection are the only commercial glasses which are essentially binary systems.

When we derived the conditions of glass formation of simple compounds[2], the rate of nucleation was the only factor which we had to consider. Now as we move into fields of more complex glasses, we find that homogeneity becomes a major factor. It is not possible to obtain a homogeneous melt which contains 80 per cent SiO_2 and 20 per cent CaO. In order to develop new glasses we have to learn first how to produce a homogeneous liquid. It is

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one object of this paper to look at the problem of making some oxides "compatible" with silica so that homogeneous melts can be obtained.

A second object of this paper is to reexamine the possibilities of obtaining glasses from combinations of oxides which by themselves are not glass formers. The preceding papers revealed that we were handicapped in our planning of new glass compositions by two erroneous limitations, namely, the requirement of a tetrahedral structure and the sharing of at least three corners of the tetrahedra. Recognizing that these conditions are basically unsound should enable us to find hitherto unknown possibilities in the development of new glasses.

We have seen[1] that none of the earlier theories could cope with the fundamental difference between the oxides V_2O_5 and P_2O_5 with respect to glass formation. The crystal chemical properties are too similar to offer a clue. Both cations, V^{5+} as well as P^{5+}, can form XO_4 tetrahedra. There is little difference in the values of the P-O and V-O bond strength, both being close to 100 kcal. The melting points of both oxides are low, 843°K for P_2O_5 and 943°K for V_2O_5. With respect to glass formation, however, the two oxides behave fundamentally different inasmuch as pure V_2O_5 cannot be obtained as a glass.

We explained this difference on the basis of the disproportioning of binding forces which dominates the melting behavior of V_2O_5. Oxides of the transition elements do not melt like silica: their melting is "defect controlled". These oxides cannot be superheated like quartz or feldspar nor can their melts be supercooled sufficiently to form glasses.

It is the second object of this paper to examine the possibilities of enforcing glass formation in systems which fail to form glasses because they develop a high concentration of defects. The last few years have taught us to cope with problems concerning the crystal chemistry of defective structures and semiconductors and we will use this knowledge in our search for additions which could alter the kinetics of melting of oxides of the transition elements so that glass formation becomes possible.

II. Compatibility Within Glass-Forming Systems

The manufacture of glass is an art which has developed on an empirical basis. Today, the scientific treatment of the empirical observations of glass technologists becomes increasingly important but even today science lags behind the art. Thus the problem of the compatibility of compounds with silica was solved empirically long before scientists became aware of it. The blending of silicates with borates was one of the milestones in the development of modern technical glasses. Analogous attempts to blend silicates with phosphates ended in failure and hence phosphates were considered to be incompatible with silicate glasses[3]. It was not until 1927 that scientists learned that even liquid silicates can be incompatible. J. W. Greig[4] in his studies of the phase relations in the binary systems $MgO\text{-}SiO_2$, $CaO\text{-}SiO_2$, and $SrO\text{-}SiO_2$ found that within certain composition and temperature regions two liquid phases were in equilibrium. The phenomenon of liquid immiscibility was found also in binary oxide systems containing B_2O_3 as one constituent[5,6].

Glass technologists are interested in the compatibility of oxides from two points of view. The incompatibility of an oxide with silica is a limitation with respect to the fields of glass formation, but, on the other hand, it is responsible for the low corrosive action of a glass on such a refractory oxide.

Compatibility requires the possibility of forming variable homogeneous composition ranges. All gases are miscible; they are compatible unless they undergo a chemical reaction. Hydrocarbons are not compatible with water whether they are gases (methane), liquids (hexane) or solids (paraffin). The fact that methane can form a hydrate does not make it compatible with water because this hydrate has to have a certain stoichiometric composition. A constant CH_4:H_2O ratio can be maintained easily in a crystal but the condition of constancy of the composition in molecular dimensions interferes with the very nature of a liquid.

A substance which is incompatible with a liquid cannot establish a concentration gradient and hence its rate of going into solution is negligible. Chromium oxide Cr_2O_3 is extremely incompatible with silica. Many glass technologist are familiar with the "black stones" which can be observed as defects if chromium compounds are introduced into the glass batch. H. Jebsen-Marwedel[7] devotes a chapter of his book on defects in glass to this particular defect. Unlike corundum or other refractory materials, Cr_2O_3 stones do not form a "tail" because they do not interact with a soda lime silicate glass in spite of the fact that Cr_2O_3 has a finite solubility and can be used for producing green glasses. In order to bring Cr^{3+} ions into solution in a glass one has to use a round-about method. A chromate may be added to the glass batch or a very finely powdered chrome ore may be used which, in contact with the alkali and the niter of the batch, forms chromate as an intermediate compound.

1. The Nature of Compatibility in Ionic Melts

Alcohol is compatible with water so that one can produce at ordinary temperature alcohol-water mixtures with a concentration range from zero to 100 per cent ethyl alcohol. This is no longer true for higher alcohols, e.g., amyl alcohol. Amyl alcohol is a liquid which at ordinary temperature can dissolve only a small amount of water and vice versa. Hence over most of the composition range two liquid phases coexist, one nearly pure amyl alcohol, the other nearly pure water. Adding ethyl alcohol to such a mixture increases the compatibility of water and amyl alcohol, making it possible to obtain a homogeneous liquid which contains substantial concentrations of both amyl alcohol and water. Amyl alcohol and water are incompatible liquids but through the proper addition of a third component they can be made compatible.

In order to form a glass on cooling, a system has to be

a homogeneous liquid. A liquid is characterized by the mobility of its particles, a feature which permits easy self diffusion, viscous flow and which also contributes to its thermodynamic stability because it increases its entropy. In order to understand the conditions which cause a system to be a liquid we need a dynamic model of its structure in addition to its thermodynamic relation to crystals.

At its melting point a crystal is in equilibrium with a liquid which has the same composition as the crystal. The crystal has a lower energy than the liquid because of the greater electrical interaction of the ions (smaller volume) and because the cations are better screened in the highly symmetrical environment of the crystal. The liquid has a lower degree of order, i.e., a higher entropy, than the crystal and at the melting point the transition of the crystal into the liquid does not change the free energy because at this temperature the energy change and the entropy change balance one another. In thermodynamics this relation is expressed by an equation which states that the free energy change of fusion is zero:

$$\Delta F_F = \Delta H_F - T_M \Delta S_F = 0$$

where

ΔF_F = free energy change during fusion
ΔH_F = heat of fusion
ΔS_F = entropy of fusion
T_M = melting point °K

The value of $\triangle S_F$ increases if a second substance is added or if the substance develops defects such as vacant lattice sites. The entropy of fusion is therefore a measure of the disorder which is introduced into a system by the melting process.

The problems which confront scientists in their efforts to develop a consistent model of a liquid are twofold. Experimentally it is the lack of a direct method which would provide a picture of the geometry of liquids which would permit a comparison with the corresponding solids. Theoretically it is the discrepancy between the magnitudes of the changes in energy and in the kinetics which are observed if a solid changes into a liquid. J. Frenkel[8], a pioneer in this field, presents this problem very clearly in his book, *Kinetic Theory of Liquids* (1946). He introduces his chapter, "Relation between the Solid and Liquid States," as follows:

"Fusion is accompanied, as a rule, by a relatively small increase of volume amounting to 10 per cent. This fact alone serves to show that the arrangement of molecules in a liquid—in the neighborhood of the crystallization point, at least—must be more or less similar to their arrangement in the corresponding solid bodies, in spite of the fundamental difference existing between the amorphous structure of the liquids and the crystalline structure of the solids (in a state of thermodynamic equilibrium).

"We must further note the well-known experimental fact that the latent heat of fusion is much smaller than the latent heat of vaporization. In the case of sodium, zinc, lead, and mercury, for example, the former is equal to 630, 1,800, 1,170, and 560 cal./mole, while the latter amounts to 23,300, 27,700, 46,000 and 14,200 respectively, exceeding thus the heat of fusion by a factor 30-40.

"This means that the cohesive forces between the molecules decrease only very slightly in the process of fusion, in agreement with the fact that their distance apart is increased by a very small figure of the order of 3-4 per cent."

The application of the K. Fajans[9] concept of chemical binding to the melting of a sodium chloride crystal[10] reveals that Frenkel's conclusion, namely, that the cohesive forces decrease only very slightly, requires a revision. Only for a perfect crystal is it meaningful to refer to the binding forces between the individual particles as having a constant value, the magnitude of which can be derived from the lattice energy. Crystals are imperfect and they become more imperfect as their temperatures are raised toward their melting points. This feature is well established. For some purposes it becomes advantageous to give a more detailed description of the nature of the defects which form in different crystals. Discussions of this subject can be found in all textbooks on the solid state. We do not need to go into these details because regardless of the nature of a particular defect it represents an asymmetry which affects the binding forces in its vicinity. Some of the binding forces within the lattice decrease and others increase in a way which no longer permits us to speak about average binding forces. It is this feature which we called the disproportioning of all binding forces into two groups of forces, one being weaker and the other stronger than the average, which makes it impossible to establish a correlation between the lattice energy and the kinetic properties. We assume that the strong binding forces produce clusters of ions which are separated by "coherent and fluctuating fissures" (weak forces). It is true that the melting process is the result of a relatively minor change of energy and volume as compared with the evaporation but it can produce drastic changes in the kinetic aspects of the system if it leads to an uneven distribution of the binding forces and the interatomic distances. Whereas in the perfect NaCl crystal each Na^+ ion is bonded to six Cl^- ions by equal forces which over a time average are constant throughout the crystal, the formation of defects changes the distribution of forces and the distances so that NaCl above the melting point consists of dense clusters of ions which are very mobile because of the "fluctuating fissures" but does not have a high vapor pressure.

The melting of most crystals is accompanied by such a change of binding forces and interatomic distances and we called this type of melting "defect controlled." There are, however, some crystals which due to the low polarizability of their ions and an exceptionally rigid coordination requirement of the cations do not permit the development of a high concentration of defects on heating. Quartz and albite (sodium aluminosilicate) are examples of crystals whose melting is not "defect controlled." The melting of these crystals can be described as a process in which the thermal motion or the kinetic energy overcomes the

average binding forces within the lattice. The melting of crystals of this type does not present the fundamental problem of having to account for a drastic change in appearance as a result of a minor change in energy and volume. The melting of an albite crystal is not accompanied by a drastic change. As a matter of fact within days the albite crystal does not change its appearance when heated to 50°C above its melting point.

Substances which melt in this fashion can be easily superheated and their melts can be easily supercooled. This type of melting favors glass formation. The alkali halides in their melting represent one extreme, albite represents the other. Most substances show a melting behavior which lies in between these two extremes.

All crystals develop defects on heating and the concentration of these defects as well as their nature depends upon the temperature and upon the substance. Scientists thinking about the structure of liquids extrapolated the formation of an increasing number of "holes" and these holes were thought to be responsible for fluidity and self diffusion.

At the time when J. Frenkel[8] developed such a concept of the structure of liquids, J. D. Bernal[11] developed a quite different model of the liquid state. According to Bernal's idea, liquids are homogeneous, coherent and essentially irregular assemblages of molecules containing no crystalline regions or holes large enough to admit another molecule.

According to our views the models of a Frenkel liquid and a Bernal liquid represent two extremes. Fused sodium chloride contains a major concentration of "holes" or as we prefer to call them "coherent fluctuating fissures" whereas fused silica and fused albite have structures which correspond closely to a Bernal liquid. Holes, in particular, anion vacancies are rare because of the rigorous screening demand of the Si^{4+} ion which does not permit a deviation from the coordination number of four. We assume that ionic liquids which form stable glasses on cooling are characterized by a low concentration of holes due to an electronic structure of their ions which is not conducive to a disproportionation of the binding forces. Liquids of this type bear a strong resemblance to "perfect" crystals a feature which we brought out in their potential energy profiles[12]. No spectacular difference should exist between such a liquid and a corresponding crystal with respect to the energy content which is vested in the short range order. The difference between such a liquid and a crystal lies primarily in the dynamics of the system because the lack of periodicity deprives the liquid or the glass of the ability to undergo cooperative maneuvers. The structural changes in such a glass are governed by statistical events. For this reason the melting of a single crystal is an irreversible process and no matter how slowly we cool its melt it cannot gradually assume a more and more ordered structure and change back into the single crystal. The inability of remote particles in a glass to cooperate makes this process impossible. Instead a highly ordered structure will form at one or more spots within the supercooled melt and crystallization will proceed as a heterogeneous reaction.

In agreement with the trend of some cations to change from octahedral to tetrahedral coordination on heating and with X-ray work on the structure of fused alkali halides we assumed that NaCl during melting undergoes a change from sixfold to fourfold coordination. Such a change of the coordination, however, is not a characteristic feature of the melting of ionic substances. Characteristic of the melting process is the mobility of the cations within the cationic part of the lattice and of the anions within the anionic part of the lattice. The mobility of the electrons in a metal does not make a metal a liquid. The metal melts if it is heated to a temperature at which the thermal energy becomes of an order which causes frequent place changes between the positive cores. Some solids, e.g., AgI, can undergo a structural change which permits a high mobility for the cations in a still fairly rigid anionic lattice[13]. Melting, however, occurs at a higher temperature where the anions also may exchange freely their positions within the anionic part of the lattice. One may say that the cationic part of the AgI lattice melts at 146°C whereas the anionic part remains rigid to a temperature above 500°C.

Lithium sulfate melts at 860°C. The monoclinic modification stable at ordinary temperature changes at 575°C into a cubic modification. According to T. Forland and J. Krogh-Moe[14] this increase in symmetry is the result of a rearrangement of the sulfate groups into a face-centered lattice which makes it possible for the Li^+ ions to move freely between the available octahedral and tetrahedral positions. Place exchange among Li^+ ions becomes rapid at 575°C but it requires 860°C in order to bring about a corresponding exchange among the SO_4^{2-} ions which is essential for changing the crystal into a liquid. It is important to realize that melting, i.e., the formation of a homogeneous liquid from a crystal, requires both a ready positional exchange among anions within the anionic part of the lattice and a ready exchange among cations within the cationic part of the lattice, but it does not require that cations may assume positions of anions and vice versa.

Thus we can describe the melting of cristobalite as a process in which the thermal energy makes it possible for the Si^{4+} ions to exchange places with other Si^{4+} ions and for the O^{2-} ions to do the same with other O^{2-} ions. The compound $AlPO_4$ is isostructural with silica and shows very close similarity in its different modifications with those of silica. A. Dietzel and H. J. Poegel[15] pointed out that the modification changes in $AlPO_4$ occur at slightly lower temperatures than the corresponding changes in SiO_2. They found, however, that this does not apply to the melting temperature which is about 2000°C for $AlPO_4$, i.e., 300°C higher than that of silica. Whereas Si^{4+} ions may exchange places above 1710°C, a higher temperature is required for Al^{3+} and P^{5+} ions to do the same. The structural similarity between the crystalline forms of SiO_2 and $AlPO_4$ is limited to the solid state

because it has to meet a rigorous geometrical condition. Each O^{2-} ion must be shared between an Al^{3+} and a P^{5+} ion, a condition which makes all O^{2-} ions common corners of one AlO_4 and one PO_4 tetrahedron. This geometrical condition in turn requires a strict stoichiometric ratio between AlO_4 and PO_4 groups namely, 1:1. It is for this reason that vitreous $AlPO_4$ which could be called an analogue of vitreous SiO_2 does not exist. At 2000°C, when Al^{3+} and P^{5+} ions become free to exchange positions, PO_4 tetrahedra can become neighbors and the system gains entropy by forming gaseous particles. P_4O_{10} molecules escape and Al_2O_3 precipitates from the melt.

The melting behavior of silica is governed by the strict coordination requirement of the Si^{4+} core with respect to its O^{2-} ions. In nature we find quartz in a very pure state because the lattice of silica does not tolerate major concentrations of foreign ions. Silica crystallizes out as pure quartz from a magma which has the very complex composition of granite. This inability of silica to form solid solutions with other oxides expresses itself in the chemical behavior of fused silica. A few oxides such as BeO or GeO_2 are soluble in fused silica because only a few cations such as the Be^{++} ion or the Ge^{4+} ion fit into its structural pattern. Most oxides interfere with the stability of liquid silica because the cations demand a coordination higher than four. Only very small concentrations of XO_6 groups can be tolerated in the tetrahedral structure of silica and the phase diagrams[16] reveal the incompatibility of most oxides with silica.

Compatibility is primarily the result of a geometrical condition. In order to be a homogeneous liquid the particles have to be able to exchange freely their geometrical positions. If this is not the case the system separates into two phases. It may precipitate a crystalline phase, form a second liquid phase, or form a gas. As far as the ability of a system to form a glass is concerned it is immaterial whether the second phase is a solid, a liquid or a gas. Any phase separation interferes with the primary condition of glass formation, namely, the supercooling of a homogeneous liquid. Fluorides are incompatible with silica because of the formation of gaseous SiF_4; chromium oxide does not dissolve in silica, it remains a solid; and for the oxides of zirconium, calcium, and magnesium the formation of a second liquid phase has been reported.

2. *Compatibility of Some Oxides with Silica*

The reaction of silica with an alkali can be described as the formation of a salt. Depending on the approach one prefers, one may say that the acidic oxide SiO_2 increases the screening of the Si^{4+} ions by surrounding them with the better screening O^{2-} ions. The O^{2-} ions of Na_2O or K_2O are better screeners because they have a higher polarizability than those of SiO_2[17].

One may use an equivalent description of this reaction which was suggested by H. Flood and T. Förland[18] according to which SiO_2 which contains O^{2-} ions of low polarizability and Na_2O which contains O^{2-} ions of higher polarizability react in order to equalize the state of polarization of all O^{2-} ions in the system.

The two descriptions of an acid-base reaction have a common denominator because the state of polarization of the O^{2-} ions is a function of the screening demand (charge, size, electronic configuration) of the cation. For this reason the two expressions are equivalent and may be used interchangeably.

Since Zachariasen[19] proposed his model of oxide glasses it has been customary to refer to an acidic oxide as a network former and to the basic oxides as network modifiers. The fundamental idea was that the structure of the glass is dominated by the coordination requirement of the network-forming cations. They are small and have high charges and consequently their electrical fields are much stronger than those of the modifying cations which are usually larger and have only low charges, one or two. There is a certain parallelism between the strength of the electrical field of a cation and the acidity of its oxide, but there is no relation between these two properties on one side and the structural aspects on the other. The electrical field of the large Th^{4+} ion is weaker than that of the small Si^{4+} ion. ThO_2 is more basic than SiO_2. The electrical field of the Mg^{2+} ions is also weaker than that of the Si^{4+} ion primarily because of the difference in charge. MgO is therefore more basic than SiO_2. The weaker electrical fields of Th^{4+} and Mg^{2+} make ThO_2 and MgO bases as compared with the acid SiO_2 but they do not impart "weakness" to structures. In spite of their weaker fields the Th^{4+} and Mg^{2+} ions in their oxides demand their screening to remain symmetrical up to much higher temperatures than the Si^{4+} ion in silica. The melting points of MgO (2800°C) and of ThO_2 (3500°C) are much higher than that of cristobalite (1710°C). Alkali borates, phosphates, and arsenates have higher melting points than the network-forming oxides. Lithium metagermanate (M.P. 1237°C) has a higher melting point than GeO_2 (1120°C)[16].

In contrast to conventional approaches to the structure of glasses we consider the geometrical requirements of all cations, even of the singly charged alkalies, as important for the formation of a glass.

The screening of the cations is a function of the number of anions which surround them, the symmetry of the resulting polyhedra, and the polarizability of the anions. Within the composition range of simple and complex technical glasses the Si^{4+} core requires screening by four O^{2-} ions which means that in a SiO_2 glass each O^{2-} ion is polarized by two Si^{4+} cores. As a result the O^{2-} ions in SiO_2 have a low polarizability and they are poor screeners for additional cations. Small additions of Na_2O, e.g., 5 mol per cent, do not permit the formation of a stable glass. Earlier we described these small additions of Na_2O as a catalyst which enhances the crystallization of cristobalite by its disproportioning of the binding forces. In a system of this composition the screening demands of the Na^+ ions are not satisfied so that vitreous silica and small amounts of alkali are not compatible; they do not form a

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homogeneous glass but precipitate SiO_2 as a crystalline phase and form a glass with a higher Na_2O content.

It is immaterial for our consideration whether the new phase is a crystal or a liquid because the compatibility of two oxides is determined by the short range order which prevails in the system. Important for us is only that in our efforts to modify silica glass we are hampered because the geometrical conditions do not permit the formation of a stable homogeneous liquid in which both the Si^{4+} and the Na^+ ions are sufficiently screened. Hence, a liquid containing 95 mol per cent SiO_2 and 5 mol per cent Na_2O does not retain a statistical distribution of the ions but separates rapidly into a siliceous phase and into one of higher than average Na_2O content. The screening demand of the alkalies increases from K^+ to Na^+ and is highest for the Li^+ ion. Hence one finds that the fields of glass formation decrease in the order of potassium, sodium, and lithium silicate glass.

If one increases the Na_2O concentration from 5 to 20 mol per cent the alkali becomes compatible with the silica and a homogeneous and stable glass can now be obtained. As a large number of polarizable O^{2-} ions become available, a new element of short range order can be established. The screening power of all O^{2-} ions is increased and the screening demands of the Na^+ ions can now be met.

The oxides Li_2O, Na_2O, and K_2O have the antifluorite structures in which each cation has the coordination number of four. However, the incompatibility of small concentrations of these oxides with silica reveals that fourfold coordination is not sufficient for screening an alkali ion if the O^{2-} ion has a low polarizability.

A mixture of 20 per cent MgO and 80 per cent SiO_2 cannot exist as a single liquid phase because the screening demand of the Mg^{2+} ion requires sixfold coordination. We have seen that the replacement of Si^{4+} ions by equal numbers of Al^{3+} and P^{5+} ions raises the liquidus temperature by 300°C in spite of both cations being able to assume tetrahedral coordination. One can imagine, therefore, that much higher temperatures are needed to make compatible two cations which not only differ in charge but also in their coordination demands. As a result such a mixture of MgO and SiO_2 forms two liquids, one having the tetrahedral structure of the pure silica and another consisting of SiO_4 tetrahedra and a sufficient concentration of MgO_6 octahedra to form a continuous anionic lattice which permits exchange among Mg^{2+} ions and exchange among Si^{4+} ions but not necessarily between an Mg^{2+} and a Si^{4+} ion. As the polarizabilities of the anions and the cations increase, this condition can be met by smaller XO_6 concentrations and, hence, the miscibility gap decreases with increasing atomic weight, size, and polarizability of the alkaline earth ions.

Most oxides which contain cations with a charge greater than one are incompatible with silica over a certain composition region. Compatibility, however, exists for some oxides (BeO, GeO_2) and develops for others when present in higher concentrations or upon the addition of a third oxide usually an alkali oxide. We shall analyze therefore, the factors which make an oxide more compatible with silica.

In the past, several attempts have been made to explain immiscibility in fused silicates. Ever since B. E. Warren and A. G. Pincus[20] gave a qualitative structural explanation for the coexistence of two liquids in the system SiO_2-CaO, scientists have tried to establish a more general and a quantitative relation which would account for the limited miscibility in some oxide systems. A. Dietzel[21] suggested approaching this problem by using the factor Z/a^2, the field strength of the cation with the charge "Z" in the distance "a" of the anions. This relation was found to be useful in structural considerations and indeed, if one plots the extent of the miscibility gap of MgO (40%), CaO (30%), and SrO (20%) versus the field strength of the cations one obtains a curve which extrapolated to the lower field strength of the Ba^{2+} ion gives a very small value for the extent of the miscibility gap. This agrees with the fact that no immiscibility has been found in the system BaO-SiO_2. However, this curve, field strength of the cation versus the extent of the miscibility gap, fails to account for the apparently complete miscibility in the system BeO-SiO_2[16].

We have to treat the immiscibility in silicate systems in a qualitative fashion because no matter which system we compare, the comparison involves the changes of too many parameters at the same time. The silica-alkaline earth oxide systems have the advantage over all other systems that the most important factor, namely, the lowest temperature at which the two liquid phases coexist, is nearly the same. However, going from BaO to MgO involves a drastic change not only in the field strength but also in the polarizability of the cation.

Any oxide which introduces into silica a cation of coordination higher than four must necessarily disturb its structure. Be^{2+} and Al^{3+} ions occur in fourfold coordination and BeO and Al_2O_3 are completely miscible with SiO_2. However, MgO, CaO, SrO, Cr_2O_3, ZnO, NiO, CoO, ZrO_2 or TiO_2 cannot form XO_4 groups in silica because in combination with the O^{2-} ions of low screening power (low polarizability) the cations introduced by these oxides demand sixfold coordination.

We can assume that the compatibility of BeO and GeO_2 with silica is the result of the ability of the Be^{2+} and the Ge^{2+} ions to be sufficiently screened by four O^{2-} ions of low polarizability. Zn^{2+} ions, too, can occur in fourfold coordination and so can Ni^{2+} and Co^{2+} ions. However, in order to be sufficiently screened by four anions these cations require O^{2-} ions of a higher screening power than those available in silica. A similar situation applies to the Ti^{4+} ions which may form TiO_4 tetrahedra in some glasses but not in combination with pure silica. R. C. DeVries, R. Roy, and E. F. Osborn[22], [16] report a fairly large region in which two liquids coexist in the system SiO_2-TiO_2. The larger Zr^{4+} is even less

compatible with silica than TiO_2, a feature which makes ZrO_2 a valuable constituent of glass tank refractories. One should expect that the extent of the two liquid region is larger in the system ZrO_2-SiO_2 than in TiO_2-SiO_2. According to the findings of N. A. Toropov and F. Ya. Galakhov[16] the two liquid regions in the ZrO_2 system is smaller than that in the TiO_2 system. However, the lowest temperature at which the two liquids coexist is approximately 500°C higher in the ZrO_2 than in the TiO_2 system. Because of the paramount effect of temperature, a comparison would be meaningless.

The phenomenon of miscibility involves the kinetics of the system. Our emphasis on the exchange of ionic positions in a liquid as the factor which determines the compatibility of an oxide with silica makes it natural to stress the importance of the polarizability of anions and cations. Describing the polarizability of a cation as its ability to adjust its electron cloud to suit different environments we can understand why highly polarizable cations are more compatible with silica than noble gas-type cations of the same size and charge. The miscibility gap in the system ZnO-SiO_2 is smaller than in the system MgO-SiO_2. It is primarily for this reason that we attributed the increasing compatibility of the alkaline earth oxides with increasing atomic weight to their increasing polarizability. The field strength of the cations is also an important factor inasmuch as it determines the state of polarization and the screening power of the O^{2-} ions which an oxide introduced into the system. Thus, for alkalies, compatibility increases from Li_2O to Cs_2O.

A homogeneous liquid which contains 85 mol per cent SiO_2 and 15 mol per cent alkali loses entropy and changes into a system which contains less probable crystalline phases on cooling. The greater the polarizability of the O^{2-} ions in such a liquid the better can it retain its more probable disordered state. Hence we find that the system remains a homogeneous liquid down to 870°C if the alkali is Rb_2O or Cs_2O. However, if the alkali is K_2O, Na_2O or Li_2O the system has to lose entropy at 1080°C, 1350°C, and 1480°C respectively.

The stability of a liquid phase is vested partly in its entropy so that the mobility of the ions is an important feature. For a constant O^{2-} to Si^{4+} ratio, as in our example, the polarizability of the anions is the most important parameter which controls the mobility. The polarizability of the anions, however, decreases rapidly if the large Rb^+ ions are replaced by smaller ions.

The thoughts on compatibility expressed here find their confirmation in the mineral kingdom. Fluorides and silica occur in very pure form and not as solid solutions. The sulfidic ore on the other hand can be of great complexity because the more polarizable S^{2-} ion can make compatible a variety of cations.

3. *Incompatibility Due to the Formation of Volatile Compounds*

We have seen that most oxides in a quantity of approximately 10 per cent are incompatible with silica; a feature which expresses itself in the insolubility of the added oxide, the formation of a second liquid, or the precipitation of cristobalite. Compounds other than oxides, e.g., fluorides, chlorides, and sulfides, can be incompatible with silica because of the formation of a volatile substance, namely, SiF_4, $SiCl_4$, and SiS_2. For some purposes it is desirable to introduce into a silicate glass fluorine (opal glasses, fluorcrown) or sulfur (cadmium sulfide glasses) and retain these compounds in the glass melt at high temperature. A glass at high temperature represents a system with a high degree of self-diffusion, i.e., cations and anions exchanging positions among themselves rather freely.

The precipitation of NaF from some opal glasses reveals a high rate of place changes even at relatively low temperatures. If this exchange of ions would be a random process which could be treated on the basis of statistics, one would arrive at the conclusion that it is not possible to retain fluorine in a silicate glass. Considering the relatively high mobility of F^- and O^{2-} ions in the striking range of an opal glass one might expect that during melting, the probability of SiF_4 molecules forming and escaping from the melt would be very high. Such a system could increase its entropy by forming mobile particles, namely, SiF_4 molecules. This raises the question:

1. How is it possible to make an NaF opal glass or why does not all of the fluorine escape from the melt as gaseous SiF_4?
2. What causes the difference between the behavior of fluorides in a soda lime silicate glass and the behavior of chlorides which cannot be retained to the same extent?

The replacement of an O^2 ion in an SiO_4 tetrahedron lowers the degree of screening of the central cation. As a result this particular silicon will improve its screening by interacting more strongly with the electron clouds of the three remaining O^{2-} ions. The Si-O bond strength increases and as a result the probability of an O^{2-} ion in an $SiFO_3$ tetrahedron to be replaced by a F^- ion is decreased. With increasing number of F^- ions the probability of further substitutions of O^{2-} ions drops off sharply so that the formation of SiF_4 molecules becomes a rare event. It is possible to retain a major concentration of fluoride ions in a soda lime silicate glass because the place changes between O^{2-} and F^- ions are not random and statistical but are governed by the tendency toward keeping the number of F^- ions in the coordination sphere of each silicon as low as possible. The same situation applies to the interaction of boron with fluorine and oxygen. BF_3 like SiF_4 is a gas.

The screening requirements of the silicon explains why and how a SiO_4 group in a melt opposes the substitution of F^- ions for O^{2-} ions. Cations such as Ti^{4+} or Ta^{5+} which have a higher coordination number than Si^{4+} ions will be less reluctant to form polyhedra in

(*Continued on page* 715)

Bibliography on Glass Structure*

PART VI

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"Theory of Molecular Structure of Sodium Phosphate Glasses," J. Am. Chem. Soc., 2, 644-47 (1950).

The sodium phosphate glasses are considered as a group, and a first approximation theory of structure is presented which is applicable to glasses throughout the entire range of composition. This treats the phosphate anions as condensation polymers with due regard being taken of the effect of ionic charge. The glasses are shown to have a three-dimensional structure which is destroyed when the glass is dissolved.

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"Physical Properties and Structure of Glasses," Glastech. Ber., 23, 297-304 (1950).

The possibilities of glass formation among oxides, sulfides and halides are investigated. The chief criteria are the rules of Zachariasen and chemical bonds between atomic constituents in the broadest sense.

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"Raman Spectra and the Structure of Glass," Cienc e invest. 6, 440-6 (1950); cf. C. A. 44, 10273g (1950).

The identification on energy frequencies of glass formers and the effect of other oxides on these frequencies confirm the non-ionic character of glass forming bonds.

183. F. W. Preston and W. H. Otto

"Evidence Against Oriented Structure in Glass Fibers," J. Soc. Glass Tech., 34, 63-68 (1950).

Heat treated glass fibers are shown experimentally to undergo contraction equally in the longitudinal and cross-sectional directions of the fiber, thus showing them to consist of isotopic material and without appreciably stronger logitudinal than transverse bonds.

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"The Nature of the Vitreous State," GLASS INDUSTRY, 32, 17-19, 77-8, 98, 123-6, 142-3 (1951).

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"The Variability of the Optical Properties and the Structure of Glass," GLASS INDUSTRY, 31, 573-5, 598, 600 (1950); cf. C. A. 44, 8609b (1950).

186. H. Cole

"Magnetooptic Effects in Glass. I. Preliminary Observations on the Application of Magnetooptic Properties of Structural Considerations," J. Soc. Glass Tech., 34, 220-37 (1950).

Verdet constants for a number of optical glasses were determined, and the plot of Verdet constants against reciprocal dispersion for all glasses, and for certain liquids and crystals, yields a smooth curve. Deviations from the simple Becquerel relation were calculated and the value magnetooptic anomaly thus obtained was correlated with the nature of the chemical bonds present in crystals and glasses. On this basis it was deduced that, particularly in Ba crown glasses, Ba can participate in the glass-network structure to a greater extent than has hereto been assumed. Similarly, La and Th in glass appear to have appreciable covalent bond character and to behave as network-forming ions.

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"D. I. Mendeleev, Originator of the First Theory of the Structure of Silicates and Glass," Steklo i Keram., 7, No. 3, 3-5 (1950).

Brief review of teachings of structure of silicates and glass by D. I. Mendeleev.

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"The Constitution of Glass," Japan Sci. Rev., Ser. I, Eng. Sci., I, No. 4, 61-6 (1950).

A hypothesis concerning the structure of glass is presented. Major points were: (1) glass consists of micells having a definite chemical composition; (2) the micells are produced in the molten state and increase in size with decreasing temperature; (3) a number of micells and their size are dependent upon thermal history; (4) the size of micells present in quenched glasses is very small and the micells are surrounded by dissociated molecules; (5) a micellular shape may be spherical, sheet like, or linear; (6) during annealing the micellular size and the distribution are changed and the alkali component in the glass is incorporated in the micells and stabilized. Physical properties such as viscosity, electrical conductivity, thermal conductivity, and transformation phenomena were treated in terms of the micell theory. It is possible to calculate properties such as thermal expansion and molar refractivity from the additive properties of the micells.

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"Structure of Silicate Glasses," J. Phys. Soc. Japan, 6, 489-94 (1951); cf. C. A. 45, 2641h, 8217f (1951).

The structure of silicate glasses is studied from an investigation of the polarizability of the O ion. The effect of the metal atoms in the network is determined from the molar refraction of the glass.

*This series will be completed next year. Reprints will be available at nominal cost, provided there is sufficient interest. Order from Reprint Dept., THE GLASS INDUSTRY, 55 West 42nd Street, New York 36, N.Y.

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The paper analyzes the general conditions for the formation of glasses, considered as polymer states with rigid irregular frameworks.

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"The Constitution of Glass," Bull. Tokyo Inst. Tech., Series B, 1 (1951).

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"Roentgenographic Structure Investigation of the Arsenic Glasses," Z. anorg. u. allgm. Chem., 266, 302-12 (1951).

The intensity curve for x-ray diffraction by the arsenic glass after the usual corrections is more like the curve calculated for a model with a claudetite structure than with an arsenolite structure, although the two calculated curves do not differ greatly. A Fourier analysis of the experimental data also indicates the structure is more like the claudetite structure. Zachariasen's rules for the structure of glasses are fulfilled by the claudetite model, but not by the arsenolite model.

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"Structure of Glass," Doklady Akad. Nauk. S.S.S.R., 76, 867-70 (1951).

Microscopic examination of glass melts and of numerous shapes of different types of glass indicates that during the period of forming and cooling of the glass melt a layer-type structure forms; this structure distributes itself parallel to the forming surface of the shape.

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"Structure of Borosilicate Glasses," J. Ceram. Assoc., Japan, 59, 474-81 (1951).

The xy_4 group formation in borosilicate glasses is discussed from the viewpoint of the ionic refraction of various oxygens in sodium borate glasses.

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199. Aniuta Winter-Klein

"Glass Formation, a General Discussion," Verres et Refrac. 6, 271-81 (1952).

Knowledge of glass is associated with the study of properties of the liquid state and of the solid state. The transition from the liquid state to the elastic solid-like through the transformation region is shown to be particularly influential upon the properties that will be exhibited by the stable glass.

Study of the liquid state indicates the conditions, structural and bond energy which appear to be required for the formation of the vitreous state.

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"The Role of Titania in Silica Glasses," J. Am. Ceram. Soc., 35, 48 (1952).

A series of glasses in the system soda-silica-titania were melted. Density measurements and refractive indices were determined. Molar refractions of the various glasses were calculated using the Lorentz-Lorenz relationship. The partial molar refraction of TiO_2 was determined in glass, corresponds closely with the values obtained from crystalline compounds and indicates that the Ti^4 ion exists in six-fold coordination. Interionic distances were calculated using the Kordes equation, the calculated Si-O distance being 1.60 A. and the Ti-O distance 2.01 A.

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"The Structure of Glass," Philips Technical Review, 13, 293-300 (1952).

Although the material "glass" has now been known for some thousands of years, the variations in which it may be obtained are not by any means exhausted. This is evident from the fact that during the last decades many kinds of glass with new properties have been developed and found applications in various technical directions. For the man of science it is gratifying to see that now, after centuries of rule in this domain, in many cases theoretical conceptions as to the structure of glass are serving as a guide to the development of new materials.

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"An Electron Diffraction Study of Some Glasses," J. Chem. Phys., 20, 1398-1400 (1952).

The interatomic spacings as obtained from the radial distribution method of analysis of electron diffraction patterns are given for vitreous silica, Vycor, and Pyrex glasses. The results are in general agreement with the x-ray diffraction results published by others.

(To Be Continued in January)

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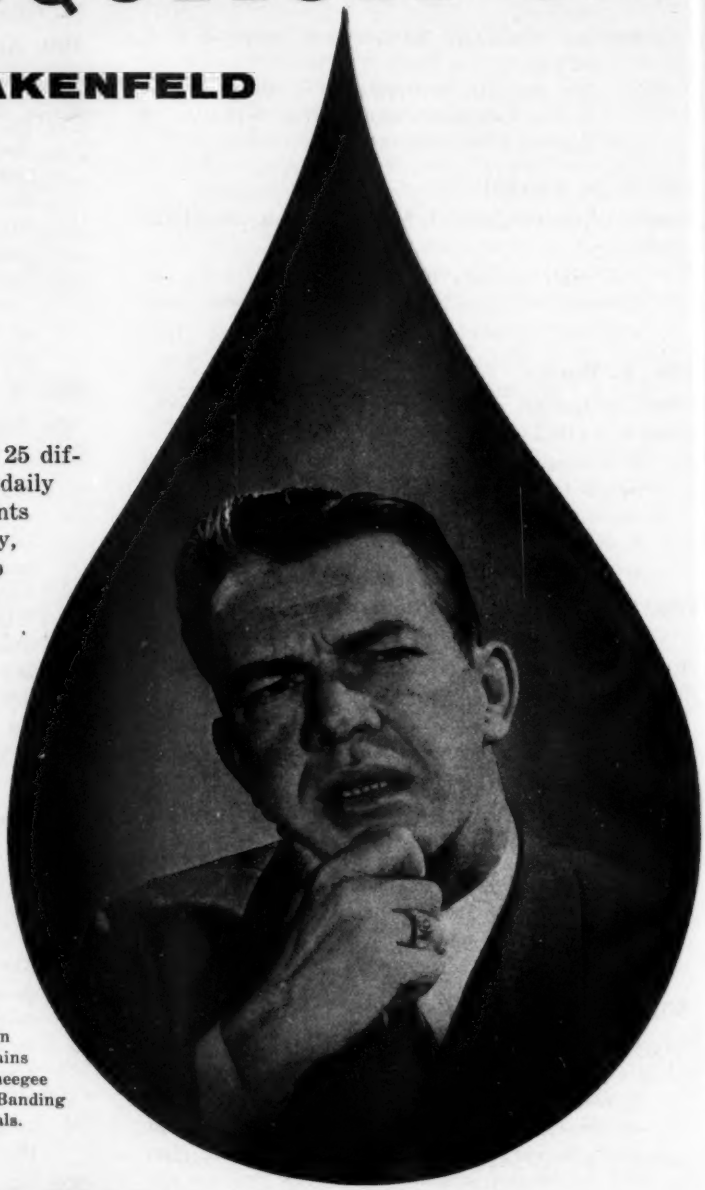

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High Modulus Glass Fibers for Structural Plastics*

by **Ralph L. Tiede,** Owens-Corning Fiberglas Corporation

The advantages offered by plastics reinforced with fibrous glass over competitive materials for many applications have come to be well recognized. However, where stiffness is an important consideration, the low modulus of glass reinforced plastics has hindered their acceptance. Since the modulus of laminates is dependent upon the modulus of the fibers, which is much higher than that of the resin, the obvious solution to this shortcoming seems to be to develop glass fibers with higher modulus.

THE PROBLEM OF DEVELOPING GLASS FIBERS with higher modulus has been the object of research activity for some time. In 1954 under Wright Air Development Center's sponsorship, the Owens-Corning Fiberglas Corporation undertook a glass composition research program with this objective. Results were reported in July, 1955.[1] This work concerned itself primarily with compositions based on calcium aluminates rather than silicates. Single filaments of the most promising glasses were produced, and these gave improved modulus values which lay between 13 and 14 million psi, as compared with "E" glass at 10.7 - 11 million. Subsequent attempts to produce fibers of this glass in a multi-hole bushing in quantities sufficient for evaluation were unsuccessful. The results of the research on glass compositions proved useful as a basis for further work, however, since they suggested that beryllium oxide might be a very effective additive to use to increase the modulus of glass. This material was not actively investigated at that time because facilities for handling it were not available.

Later, Capps & Blackburn[2] of the Bureau of Standards prepared and studied a large number of glasses and verified the prediction that beryllium oxide could be effective in raising the modulus. Although they were able to produce a few filaments in a one-hole bushing, none of their glasses appeared to be operable in commercial multi-hole bushings.

Selection of Compositions

With the background in the effect of composition changes on modulus afforded by these two investigations, it is possible to make some generalizations concerning the effects of various oxides.

1. Oxides of elements from Group I in the Periodic Table decrease modulus, the effect increasing with increasing molecular weights. Only lithium oxide is tolerable in significant quantities. Sodium and potassium oxides, widely used in commercial glasses, can scarcely be considered.
2. Oxides of elements from Group II tend to be beneficial in raising modulus, the effect decreasing with increasing molecular weights. Beryllium oxide appears to be the most effective material known for raising modulus.
3. Of the Group III oxides, boric oxide lowers modulus, whereas aluminum oxide is fairly effective in raising it.

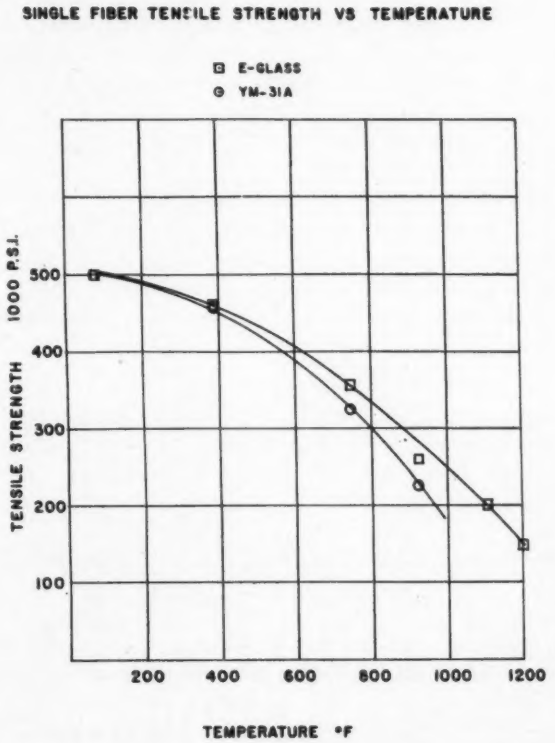


Fig. 1.

*Presented at Wright Air Development Division, Dayton, O., Oct. 12, 1960.

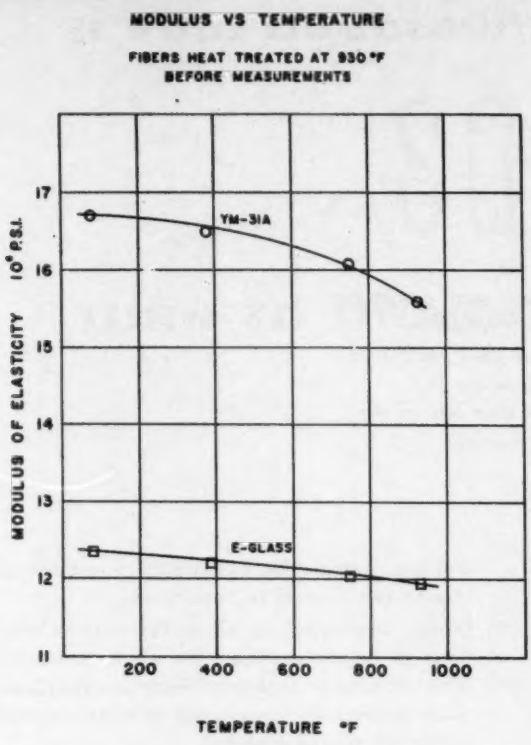


Fig. 2.

4. The silica content should be kept as low as possible for minimum modulus. Pure silica fibers have a modulus slightly under that of E-glass.
5. Certain oxides have relatively little effect on modulus, but may be quite effective in modifying other glass properties. Those found most useful in this respect include the oxides of titanium, zirconium, cerium, zinc, tin, iron and copper.

Properties Required for Forming Fibers

Many factors other than the modulus must be considered in selecting a glass for the production of fibers. Any commercial glass composition is a compromise between various factors, and very rarely does a composition change influence all of them in a desirable direction.

1. *VISCOSITY - TEMPERATURE RELATIONSHIP.* The viscosity of a glass decreases as the temperature is raised. Fibers can be commercially drawn only in a certain viscosity range. This viscosity must be attained at a temperature low enough to permit the use of materials available for construction of the forming apparatus. For conventional forming processes, this means platinum alloys. On the other hand, since the maximum service temperature of the fibers in use is related to viscosity, the glass must not have a low viscosity at too low a temperature. The rate of change of viscosity with temperature is important, too, since it has a bearing on the degree of temperature control and uniformity required to produce fibers of acceptable quality.

2. *LIQUIDUS OR DEVITRIFICATION TEMPERATURE.* If held for sufficient time in a certain temperature range, any glass will undergo a process called devitrification, in which some crystalline phase separates out from the melt. The time involved before this occurs may vary from a few seconds to days, depending upon the glass composition. The liquidus, the highest temperature at which devitrification can occur, is a fixed temperature for any given composition, and is characteristic of that composition. It is desirable to use a glass with a liquidus temperature as low as possible. Fiber forming must obviously be carried out at temperatures above the liquidus to prevent the formation of crystals which would interrupt the process by causing fibers to break. A high liquidus, like a high viscosity, requires a high operating temperature, with the associated difficulties due to the limitations of materials available for construction of the forming apparatus.

3. *LIQUIDUS-VISCOSITY RELATIONSHIP.* As mentioned previously, fiber forming must be done in a given viscosity range. A glass in which devitrification occurs in this range cannot be successfully formed into fibers because the crystals will cause interruptions. If the temperature is raised in an attempt to get above the liquidus, surface tension causes the formation of beads instead of fibers. If the temperature is lowered, the fibers break because of too much mechanical tension.

4. *DEVITRIFICATION RATE.* It is desirable to have a glass which devitrifies slowly, since it gives more latitude for fluctuations in temperature within the forming unit.

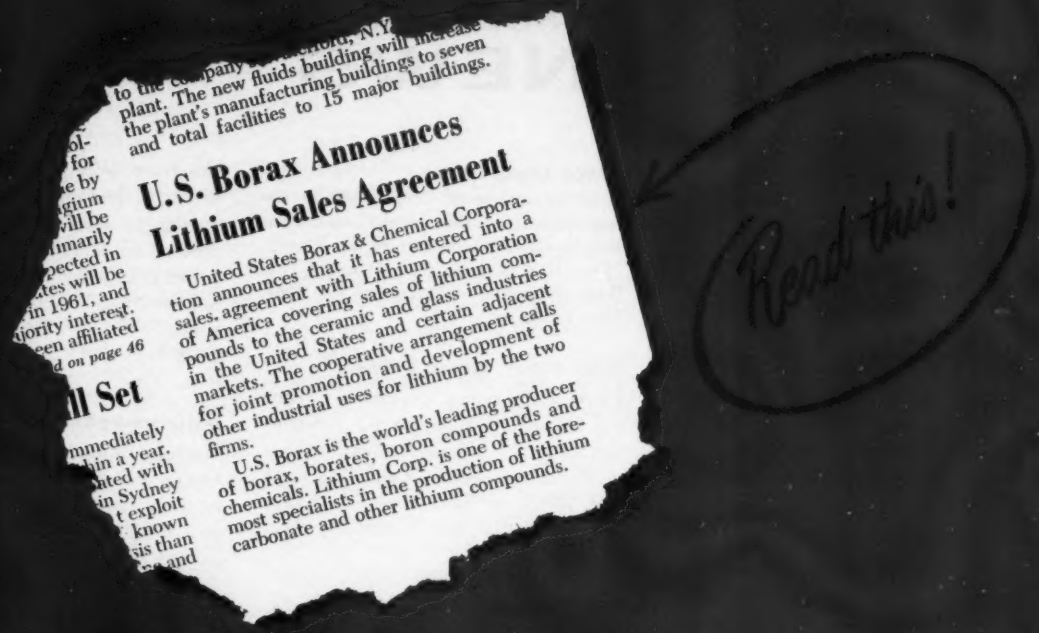
5. *CHEMICAL DURABILITY.* The small diameter and high surface to volume ratio for glass fibers impose extreme chemical durability requirements on the glass from which they are made. The ordinary soda-lime glass of commerce serves very well for windows, jars, bottles, etc. It can be made into fibers, too, but the difficulties associated with protecting it from attack by the moisture in the air are such that little commercial use is made of it. Any suitable glass must have adequate durability for storage, handling and eventual satisfactory performance in plastics or other end uses. In addition, the glass must be compatible with whatever size, finish or coating that must be applied during processing into a useful product.

6. *COST.* Materials and fabrication costs are ever-present considerations. When beryllium oxide is a factor, costs are necessarily higher because of both higher raw material and processing costs.

Development of YM-31-A

Sixty-two experimental glass compositions selected on the basis of the before-mentioned considerations were evaluated by Owens-Corning Fiberglas in the final effort

(*Continued on page* 717)


plant. The new fluids building will
the plant's manufacturing buildings to seven
and total facilities to 15 major buildings.
U.S. Borax Announces
Lithium Sales Agreement
United States Borax & Chemical Corporation announces that it has entered into a sales agreement with Lithium Corporation of America covering sales of lithium compounds to the ceramic and glass industries in the United States and certain adjacent markets. The cooperative arrangement calls for joint promotion and development of other industrial uses for lithium by the two firms.
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NEWS

Norman F. Heydinger

And Robert L. Morgan have been appointed manager of marketing services, and manager of woven textile marketing, respectively, at Pittsburgh Plate Glass Company's Fiber Glass Division.

Edwin M. Lindsay

Assistant to the director of research, Owens-Corning Fiberglas. He was formerly the facilities Manager for the Cornell Aeronautical Laboratory.

Wolfgang C. Forster

And James E. DeFoor have joined Modiglass Fibers, Inc., as manager of technical service, and manager of textile products, respectively.

New Distributors

Johns-Manville has appointed Ribelin Distributors, Inc., with offices in Dallas and Houston; Northwest Fibr-Glass Company, Minneapolis; and Associated Industries, Inc., Wichita, as new distributors for its fiber glass roving and chopped strand mat, which are used in fiber glass-reinforced plastic products such as boats, translucent panels, sports equipment, tote boxes, trays, and similar items.

Gustin-Bacon Mfg. Co.

Ended the fiscal year, September 30, with new highs in sales and earnings. The sales gain amounted to 11.5 per cent and profits rose 16.6 per cent over the preceding fiscal year.

Net sales in the fiscal year were $31,947,869, compared with $28,656,908 a year earlier. Net income was $2,426,-865 compared with $2,082,386.

The company began a large expansion program during 1960 to provide facilities for entering into new fields and expanded product lines.

Some of the new equipment includes a new centrifugal process for manufacturing insulation for homes and household appliances; an electronically controlled automatic batch-making facility to supply the requirements of the enlarged plant; and equipment to produce textile-type glass fibers for the reinforced plastic industry.

Fiber Glass Boats

Are the products concerned in the negotiations of the Love Corporation, Henderson, Tex., to acquire the Amphibious Boat Corporation, Denton, Tex. Both companies manufacture the glass fiber craft.

New Fiber Glass Plant

Ferro Corporation, Nashville, Tenn., has announced plans for the construction of a $2.5 million industrial plant in Huntington Beach, Calif. The move will place the firm close to Orange County, Calif., and a growing boat industry.

H.I. Thompson Fiber Glass Co.

Declared the regular quarterly dividend of 8 cents a common stock share, plus a 25 per cent stock dividend.

Reichhold Chemicals

Has increased its ownership of Modiglass Fibers, Inc., to approximately 95 per cent, by exchanging common stock shares with Modiglass.

Fiber Glass Firms Merge

Molded Fiber Glass Body Co., Ashtabula, O., and the Molded Fiber Glass Tray Co., Linesville, Pa., will merge effective January 1. The surviving concern, Molded Fiber Glass Body Co., will exchange 1 2/10 shares of its stock for each share of Molded Fiber Glass Tray Co. There are 149,595 outstanding shares of Molded Fiber Glass Body and 26,536 outstanding shares of Molded Fiber Glass Tray. The companies' 1960 sales will run between $11.5 and $12 million.

Tee-Pak, Inc.

Has been appointed a national distributor, by Goodyear Aircraft Corporation, of reinforced plastic food handling bins and allied products for the meat packing and food processing industries.

The one-piece fiber glass-reinforced plastic bin is molded in a 700-ton press. It was developed by Goodyear for storing, curing, shipping or sorting meat and meat products. Because of their resistance to corrosion and deterioration, the bins are estimated to have saved the meat packing industry more than a million dollars since their introduction in 1958. They have been approved for distribution to the meat packing industry by the Meat Inspection Division, U.S. Department of Agriculture, and by the American Meat Institute.

Miller-Stephenson

Chemical Co., Inc., South Norwalk, Conn., distributor-producer of epoxy products and adhesives, polyester resins, and fiber glass cloth and mat, has opened a new sales and warehouse in Boston at 99 Chauncy street.

Fiber Glass in Transportation

By 1965, one-fifth, or approximately 105 million pounds, of the anticipated output for the reinforced plastics industry is expected to be used by the transportation industry, according to Clare E. Bacon, Owens-Corning Fiberglas Corporation.

Speaking at the annual meeting of the Truck Body and Equipment Association in Chicago, Mr. Bacon predicted that fiber glass reinforced plastics will become the major construction material in truck-trailer-bus fabrication within a few years.

He reported that the Heil Company, fabricator of a one-piece molded milk truck tank, has laboratory tested some reinforced plastic panels in the field of ultra-low temperatures — cryogenics. The results indicate that fiber glass reinforced plastics can provide an economical method of transporting atmospheric gases by cooling them to liquid form, so much greater quantities can be carried in a smaller space. Transportation of liquefied gases at extremely low temperatures, particularly liquid oxygen and hydrogen rocket fuel, is now a requirement of the military. By far the best type of solid wall insulation for this application, fiber glass reinforced plastic skins molded around a cryogenic foam material have achieved "k" factors in the range of .06 B.T.U.'s per hour, per square foot of surface area, per inch thickness, at liquid nitrogen temperatures of minus 320°F.

Applications...

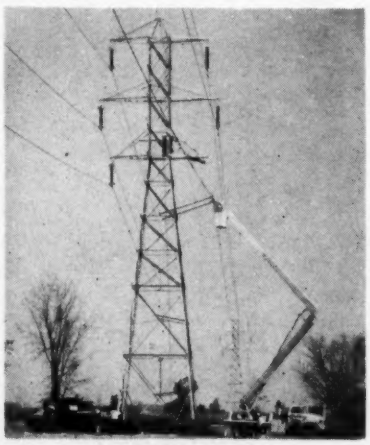
FIBER GLASS BASKETS aid lineman to work barehanded (Fig. 1) on power transmission lines carrying voltages up to 380,000 volts.

The new method of maintenance utilizes the principle that current does not flow when there is no difference in voltage between two points.

Philip Sporn, president of American Electric Power Service Corp., where the technique was tested and is about to be adopted as standard practice, likens the method to birds perching on electric wires. "They can perch on

(Fig. 1)

electric wires, even high-voltage lines, with nonchalance because they are not in contact with the ground. When they alight on a wire, they merely become charged or energized to the voltage of the line itself, and in this process they are not even hurt." Like the birds, the lineman is not even physically aware that he is energized to the same voltage as the wire.



(Fig. 2)

The linemen stand and work in a fiber glass bucket which is hoisted to overhead wires by a truck-mounted, insulated aerial boom. A metal screen lines the inside of the bucket, and is connected by clamps to the hot wire on which the men are working. Thus, the mesh is energized at the same voltage, as are the linemen. The insulated boom protects them from the difference in voltage between the ground and the live conductor.

Extensive tests have been made to verify the safety of the operation. The most recent was carried out on a 138,000 volt steel tower transmission line near Findlay, Ohio. (Fig. 2)

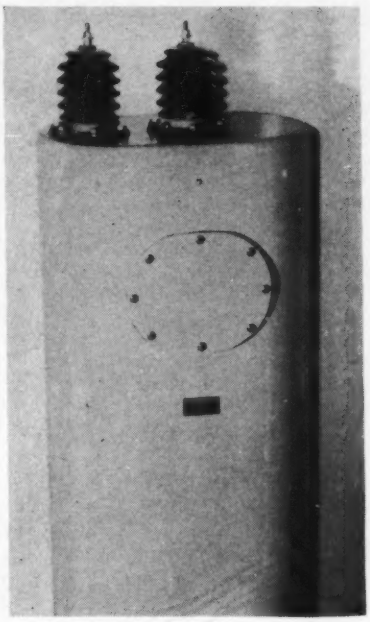
The method provides reduced line maintenance costs by saving time and manpower; insures service continuity by eliminating interruptions for line repairs; and in many cases assures greater safety than the use of live line tools in conventional practice.

Harold L. Rorden, high-voltage practices engineer for American Electric Power, developed the basic idea and supervised the research and testing, assisted in the development work by Merle L. Fisher, transmission superintendent, Ohio Power Co. The laboratory work was carried out in the Ohio Brass High-Voltage Laboratory, Barberton, O., with the assistance of Holan Corp., Cleveland, O.

Development of Technique: American Electric Power Service Corp., 2 Broadway, New York 8, N.Y. Testing and Equipment: Holan Corp., 4100 W. 150th St. Cleveland 11, O.

FIBER GLASS ANTENNA TRUNK has been approved by the Maritime Administration of the U.S. Department of Commerce. Among the ships using or planning to use the trunk are: GTV William Patterson, an experimental gas turbine converted Liberty ship; N.S. Savannah, world's first nuclear-powered merchant ship; and Surveyor, the U.S. Coast and Geodetic Survey's new hydrographic vessel.

The fiber glass reinforced antenna trunk is said to provide increased operating efficiency and greater safety while eliminating extensive maintenance problems posed by metal units. The unit is



7 ft. 4 in. high, 25 in. wide, 15 in. deep, and weighs 200 pounds. The cost is only two-thirds that of a steel trunk. A 40 ft. whip antenna can be mounted through the top of the trunk replacing the horizontal antenna.

Design and Development: Texaco Experiment Inc., Richmond, Va., subsidiary of Texaco Inc., New York; Mobjack Mfg. Co., Gloucester, Va. Antenna: Marine Div., of Mackay Radio and Telegraph Co., Inc., Clark, N.J.
Resin: Durez Plastics Div., Hooker Chemical Corp., N. Tonawanda, N.Y.

Fiber Glass Booklet

A letter-sized booklet, just published by the Reinforced Plastics Division of The Society of the Plastics Industry, Inc., describes the six basic techniques that the reinforced plastics industry uses to mold an array of products.

The molding techniques described are hand lay-up, spray-up, matched metal die preform, premix, filament winding, and pre-preg. The specific advantages and applications of each method are included, as are the physical and chemical properties of parts molded by each method.

The booklet may be obtained without charge by writing to the Reinforced Plastics Division, The Society of the Plastics Industry, Inc., 250 Park Ave., New York 17, N.Y.

Season's Greetings
Our sincerest wishes for a HAPPY YULTIDE season ... laden with love, warm friendship and good fellowship.
May the spirit of peace on earth to men of good will prevail during the coming YEAR
... and may health and prosperity be yours.

THE O. HOMMEL CO.

Dept. GI-1260 PITTSBURGH 30, PA.

West Coast — 4747 E. 49th Street, Los Angeles, California

HOMMEL

NEWS
IN THE GLASS INDUSTRY

Personalities...

Joseph T. Owens

Joseph T. Owens

Elected vice president, Pittsburgh Plate Glass Company. He will continue to serve as general counsel and secretary.

Cyrus V. Anderson was elected associate general counsel for the company.

Thurman E. Brown

Director of development, Columbia-Southern Chemical Corporation's research and development laboratory, Corpus Christi, Tex.

James L. Young

Chief inspector, Hartford Division, Emhart Manufacturing Company.

Stanley J. Solek succeeds him as supervisor-inspection.

James M. Hait

President, Food Machinery and Chemical Corporation, formerly executive vice president in charge of the company's ordnance division and also director of engineering.

Robert P. Bamford

Joined Libbey-Owens-Ford Glass Company's field sales division. He will be assigned to Seattle, Wash. Other new members of the division include: John Caroline, Jr., assigned to Los Angeles; Thomas B. Gannett, Jr., assigned to New York; Brian L. Johnson, assigned to Richmond, Va. and Richard G. Mercner, assigned to Philadelphia.

Glass Division Awards

C. L. McKinnis, Owens-Corning Fiberglas Corporation and J. W. Sutton, Boeing Aircraft Corporation received the 1960 Frank Forrest Award at the fall Glass Division meeting, American Ceramic Society, Bedford, Pa., for their studies on the nature of glass melting processes.

Robert Gardon, Pittsburgh Plate Glass Company, won the 1960 S. B. Meyer Jr. Award for studies on temperature distributions in glass undergoing heat treatment.

August C. Siefert, Owens-Corning Fiberglas Corp., trustee of the Glass Division, presented the awards.

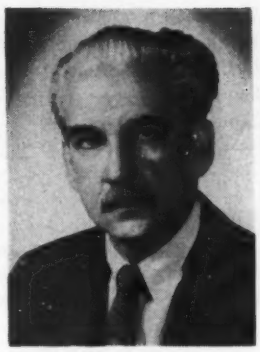
Charles W. Bowden, Jr.

Industrial sales manager, International Division, Minneapolis-Honeywell Regulator Company. Succeeding him as advertising and sales promotion manager of Philadelphia-based division is Arthur O. Dietrich.

William T. Graff, Jr.

And T. G. Braithwaite, formerly on the Tygart Valley Glass Company sales staff, have joined Brockway Glass Company's sales organization.

William D. Borland has been transferred from the Buffalo to the Chicago sales office and Charles O. Krouse, from the Food Sales Division to the Cincinnati sales office.



Dominic D'Eustachio

Dominic D'Eustachio

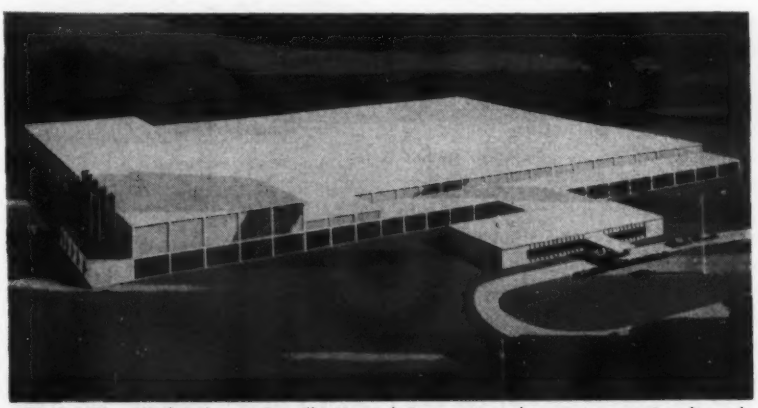
Director of research, The Pittsburgh Corning Corporation. He has been the firm's chief physicist since 1956, and now succeeds Dr. A. H. Baker, who will continue in a full-time consulting capacity.

Elmer A. Lundberg

Elected president of the Producers' Council, an affiliate of the American Institute of Architects. He is the director of architectural services for Pittsburgh Plate Glass Company.

Benjamin F. Bastian

Plant engineer of Armstrong Cork Company's glass container plant in Dunkirk, Indiana, succeeding Joseph T. Martin, who has retired.



Corning Glass Works' plant at Danville, Va., is being constructed to meet a growing demand for high quality specialty glasses used in laboratory, industrial and electronic applications.

Predicts Car Sale Hike

The chairman of General Motors Corporation, Frederic G. Donner, predicted that Americans will buy 8,000,000 new cars and 1,500,000 new trucks a year by the end of this decade.

Basing his forecast on a growth in the gross national product from $500 billion this year to $700 billion in 1970, Mr. Donner said the increase will lead more and more families to own two cars, and will mean at least one car for an increasing proportion of all families.

Laurence A. Keim

Manager of technical service, automotive sales, for the Glass Division of Pittsburgh Plate Glass Company.

John L. Collins

Manager of plant and process engineering, Consumer Products Division, Corning Glass Works. Alfred C. Kerschensteiner was named staff manufacturing engineer for the company's Engineering Division.

Charles L. Goss is now product manger for Corning's New Products. Division.

In the Technical Products Division, Frederick F. Fleischman, Jr., was named district sales manager of the newly created Pittsburgh office. William M. Baldwin is manager of market development for the Lighting Products Division . . . Robert T. Cahill is manager of sales service for the Division . . . Robert C. Reese is supervisor of product engineering for the plant equipment sales department.

Charles J. Sindlinger

Manager of the planning department, Columbia-Southern Chemical Corp. He succeeds Frances A. Theis, recently elected president of Pittsburgh Plate Glass International, S. A. Both companies ar subsidiaries of Pittsburgh Plate Glass Company.

William F. Kiefer

Manager of Corning Glass Works' new Danville, Va., plant. Mr. Kiefer is now manager of the company's Australian operations at Sidney, Australia, and will be succeeded there by William M. Hodgins, presently controller at Sydney.

John R. Freeman has been appointed production superintendent at the Danville operation.

Companies...

Binswanger Glass Co.

Will complete work on its Port Arthur Tex., facilities by January 1. Expansion of the company's operations at Meridian, Miss., were completed last month.

American-St. Gobain

Began construction on its $40 million plate glass plant near Kingsport, Tenn. Covering almost 23 acres, the operation will produce 40 million sq. ft. of quarter-inch thick plate glass annually; enough to pave a one-lane highway stretching from New York City to Kansas City.

Every day after it is completed, a furnace, fired by three million cubic feet of natural gas, will convert 330 tons of sand, soda ash, dolomite, limestone, feldspar, and salt cake into a continuous ribbon of glass 130 inches wide. As the glass moves over the first 1,000 feet of roller bed it will be cooled, inspected for flaws, and ground smooth on both sides. At the thousand-foot mark, the glass ribbon will be cut into large sheets. Then the sheets will roll another 800 feet as they are buffed to a finish by felt pads.

The grinding machines are cast iron discs, 150 inches in diameter, which simultaneously grind the glass on both sides with specially graded sand. They exert approximately 350 pounds of pressure per square foot.

In addition to the plant, other elements of the construction job are a pumping station which will boost 3,000,000 gallons of water daily from the Holston River to the plant, a slurry pond to settle the sand used in grinding and the iron oxide used in polishing out of the water, and an outlet to return the water to the river.

The plant site provides proximity to raw materials, low cost power, and convenient rail and truck access to the nation's leading markets. Since Kingsport is also the site of the company's Blue Ridge Division, the new plant's location will enable the company to effect economies in manufacturing costs. Shipments of raw materials and finished products at the plant will amount to nearly a half-billion pounds per year.

A permanent office building, to be erected later, has been designed as a showcase for the uses of architectural glass.

The plant was designed by Compagnie de Saint-Gobain of France. H. K. Ferguson Company, Inc., Cleveland, is the engineer for the project.

Armstrong Cork Company

A major expansion program, begun in late November, will substantially increase the manufacturing capacity of Armstrong Cork Company's glass container plant at Millville, N. J.

Two glass furnaces will be re-built to gain a 40 per cent capacity increase in each.

The project also includes: conversion of three four-section I.S. forming machines to two six-section machines; installation of modern instrumentation for tank operating control, new furnace valve system for greater efficiency, and special feeder equipment for high-speed production of light-weight containers.

Another furnace at the plant has already been re-built and enlarged, increasing its melting capacity by 35 per cent.

Harbison-Carborundum Corp.

Added a new electric arc melting furnace to the research facilities at Falconer, N.Y. The furnace is capable of developing pouring temperatures up to 4500°F. The unit provides a research tool for use in heat and corrosion-resistant applications in the glass industry.

Owens-Illinois Glass Co.

Began producing face plates for 19- and 23-inch television picture tube bulbs at their Muncie, Ind., plant in order to meet the increased demand for the product. Equipment is currently being installed for producing funnels for the tubes. Also at the Muncie plant, a second furnace was re-opened to manufacture glass block and Thinlite glass curtainwall.

Production has begun at the company's new glass container plant in Bogota, Colombia, and substantial sales gains were registered in many of the company's container products.

63rd A.C.S. Annual Meeting

The American Ceramic Society, Inc. will hold its 63rd Annual Meeting at the Royal York Hotel, Toronto, Canada, April 23-27. The Glass Division program will consist of papers of general interest on glass, and a symposium on Nucleation and Crystallization Phenomena in Glass and Melts. Both the Glass and Basic Science Divisions are sponsoring the symposium. Deadline for titles and abstracts is January 15, and the deadline for manuscripts is February 15. Authors intending to submit papers of general interest should contact Chairman, C. L. Babcock, Owens Illinois Technical Center, Toledo 1, O. for copies of the program form, which, when properly filled out should reach the program chairman by January 1. Anyone intending to submit manuscripts for the symposium should contact Guy E. Rindone, Pennsylvania State University, University Park, Pa.

Optical Society—Spring Meeting

The 1961 Spring Meeting of the Optical Society of America will be held in Pittsburgh, Pa., March 2, 3, and 4, in part concurrently with the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy.

New Frontiers in Optics and Spectroscopy will be the topic of a jointly-sponsored symposium to be held Thursday morning, March 2. It will consist of the following invited papers.

Optical and Infrared Masers. By Charles H. Townes, Institute for Defense Analyses.

Spectroscopic Studies in the Thermonuclear Field at the Oak Ridge National Laboratory. By J. R. McNally, Jr., (and co-authors) Thermonuclear Div., Oak Ridge National Laboratory.

New Frontiers of Astronomical Optics. By A. B. Meinel, Kitt Peak National Observatory.

Others areas to be covered by invited papers are: Optics in Japan; Optical Workshop Practice; and Modern Methods of Lens Design.

It is hoped the invited papers will encourage contributed papers. To present a contributed paper, the author must submit the title plus an abstract (no longer than 200 words), in duplicate, on a standard abstract form to: Optical Society of America, Executive Office, 1155 Sixteenth St., N.W. Washington 6, D.C. Attn: Mary E. Warga.

There will also be exhibits covering instruments in the areas of optics, emission spectroscopy, ultraviolet, infrared, mass spectroscopy, fluorescence, spectrophotometry, and spectrochemical analysis.

Ford Motor Co.

Ignited the gas jets for a new 1,350-ton plate glass furnace at the company's Nashville, Tenn., glass plant. Capable of producing 400 tons of glass daily, the furnace will double the plant's plate glass capacity.

The heating and gradual filling of raw materials requires approximately three weeks, and, according to the present schedule, the first glass will be drawn on December 16.

The new furnace and its housing, a 121,000 sq. ft. addition to the east side of the plant, are part of a multi-million dollar expansion project. Another facet of the program is a new sheet furnace, now nearing completion, which will be fired in April. It will be housed in a separate 67,000 sq. ft. building. These two furnaces will boost plant employment by about 220 persons.

The expansion also includes a new windshield shipping and storage area with 38,000 sq. ft. of floor space, and an added 48,000 sq. ft. of storage space near the existing and new furnaces.

Optical Society Meets

The Society's annual meeting was held in Boston, October 12-14, and featured papers covering optics in space and rocket research, fiber optics, and image formation. A series of four papers designed to bring together work of an optical nature, primarily wave propogation, comprised a three-hour seminar.

FINANCIAL DATA

(Nine Months Ended Sept. 30, 1960)

American Potash & Chemical Corp.

	1959	1960
Net earnings	$ 3,805,555	$ 3,745,192
Net sales	$41,242,331	$38,250,153

Brockway Glass Co.
(end fiscal year)

	1959	1960
Net earnings	$ 3,507,947	$ 3,048,250
Net sales	$53,729,443	$52,632,661

Corning Glass Works

	1959	1960
Net earnings	$ 17,944,084	$ 17,580,333
Net sales	$147,717,908	$165,481,036

Diamond Alkali Co.

	1959	1960
Net earnings	$ 8,335,939	$ 9,226,861
Net sales	$103,327,519	$107,741,492

Emhart Mfg. Co.

	1959	1960
Net earnings	$ 1,260,363	$ 2,096,339
Net sales	$19,519,900	$24,311,302

Foote Mineral Co.

	1959	1960
Net earnings	$ 1,116,252	$ 501,578
Net sales	$16,494,229	$13,188,597

Owens-Illinois Glass Co.

	1959	1960
Net earnings	$ 32,244,447	$ 26,653,395
Net sales	$426,731,588	$430,707,387

Pittsburgh Plate Glass Co.

	1959	1960
Net earnings	$ 34,064,967	$ 38,101,121
Net sales	$446,248,355	$482,217,227

Thatcher Glass Mfg. Co. Inc.

	1959	1960
Net earnings	$ 2,023,118	$ 1,173,489
Net sales	$39,652,673	$39,318,603

Wyandotte Chemicals Corp.

	1959	1960
Net earnings	$ 1,166,000	$ 1,597,000
Net sales	$26,780,000	$27,141,000

NEW APPLICATIONS IN GLASS...

Aircraft Windshield

Double-glazed and laminated glass for aircraft windshields has been tested to withstand the impact of a 4-pound bird hurled at a speed of 400 miles per hour. The center windshield for a jet aircraft cockpit is composed of two laminations separated by an air space.

The outer lamination consists of an outboard piece of $\frac{7}{16}$-in. plate glass, $\frac{3}{8}$-in. polyvinyl butyral plastic interlayer, and an inboard light of $\frac{1}{2}$-in. plate glass. The inner unit has a layer of $\frac{1}{8}$-in. glass, a $\frac{1}{4}$-in. interlayer of plastic, and $\frac{3}{8}$-in. glass for the inboard light. This unit is electrical conducting glass and provides a heat range of 85° to 110°F. which gives the relatively thick plastic interlayer a soft and resilient character. Under impact the glass may fracture but the resilient and tough plastic absorbs the impact and doesn't rupture, preventing a breakthrough. The glass also safeguards against ice, frost, and fog.

The electrical conducting facility of the glass is provided by a metallic film placed upon the inner unit of glass. This glass is laminated inside the complete structure for ordinary surface protection and to minimize wear and tear.

Glass: Libbey-Owens-Ford Glass Co., 811 Madison Ave., Toledo 1, O.

Mirrors for Precision Telescope

The 60-inch astrometric telescope to be constructed at the U.S. Naval Observatory's Flagstaff Station, Flagstaff, Ariz., will use two giant mirrors of fused silica, one the largest ever made—62-inches in diameter. The other will be a 35-inch piece.

This is the first large reflector telescope designed expressly for astrometric work. The instrument will aid in determining distances and motions of faint stars up to 100 light years away, or 600 trillion miles from the solar system. Man's ability to measure the motion and determine the position of celestial bodies, natural and artificial, will be increased a hundred times.

Mirror Blanks: Corning Glass Works, Corning, N.Y.

New LOF Building

Libbey-Owens-Ford Glass Company's new 15-story office building in Toledo, O., is another example of the growing market for glass in architecture. The building exterior is approximately 90 per cent glass, consisting of 78,496 sq. ft. of Thermopane and Vitrolux.

The structure utilizes the "curtain wall" type of construction, where steel frameworks, not the glass skin of the building, carry the building load.

Curtain wall construction is generally associated with skyscrapers and large office buildings, but this style of architecture is also used for schools, hospitals, libraries, laboratories, restaurants, shopping centers, motels and theaters, bus and air terminals, and, recently, the new mechanized post office in Rhode Island.*

Speed and economy of erection are main advantages of curtain wall construction, as well as greater usage of floor space, a more pleasing appearance and reduced maintenance.

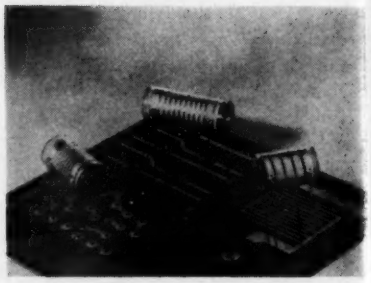
Glass: Libbey-Owens-Ford Glass Co., Toledo, O.

Corrosion Resistant Glass

A new glass said to be the most corrosive-resistant glass ever applied to steel products is now standard on Glascote's linings for reactors, vessels, columns, storage tanks, rotary dryer-blenders and coating agitators for the chemical, plastics, pharmaceutical and related industries. Outstanding field experiences and positive customer reaction have been responsible for the decision.

Glass: A. O. Smith Corp., Glascote Products, Inc., Cleveland 17, O.

*See THE GLASS INDUSTRY, Nov., page 651.



Fixed Glass Inductors

Glass inductors with wire leads are being produced for circuit board mounting. Because silver metallized conductors are fired into special glass coil forms, the inductors are said to have superior stability under physical shock, vibration and temperature change.

Glasses: Corning Glass Works, Corning, N.Y.

Calibrating Glass

New kind of glass provides a method for quick and precise calibration of recording spectrophotometers for wavelength accuracy. The glass is formed by a combination of the rare earth element holmium and a special glass that transmits radiant energy in the ultraviolet region of the spectrum between 200 and 300 milli-microns. The transmission spectrum of the glass shows a wide range of sharp absorption bands well-spaced through the ultraviolet, visible, and near-infrared. This constant definitive quality gives the glass its outstanding calibrating characteristics.

Glass: Corning Glass Works, Corning, N.Y.

CATALOGS RECEIVED

Glass blocks and sculptured glass modules. (20 pages) Sets forth technical data on light transmission, insulation value, physical performance and proper selection of block. Detailed drawings of typical glass block elevations and sections, and their construction are displayed. The design flexibility and functional advantages of both blocks and modules are discussed.

PITTSBURGH CORNING CORP., One Gateway Center, Pittsburgh 22, Pa.

General Electric Molybdenum glass melting electrodes now available from stock!

G-E electrodes are taken from stock (above), cleaned, cut to the length ordered, and shipped.

You can get fast shipment and at the same time decrease your stock investment. General Electric is ready today to ship 1¼" Glass Melting electrodes from "on the shelf" warehouse stocks.

With expanded manufacturing facilities now in full operation, General Electric can deliver these electrodes with amazing speed.

In addition, you receive a top-quality product. General Electric molybdenum glass melting electrodes are practically carbon-free—less than 50 parts carbon to *1 million* parts molybdenum! This high degree of purity provides excellent resistance to the action of molten glass.

Other features which help make G-E electrodes an ideal product for glass melting: **1. High melting point. 2. High temperature strength. 3. Good thermal shock resistance. 4. No thermal transformation. 5. Good electrical conductivity. 6. Low coefficient of thermal expansion.**

Order "sintered" and worked General Electric molybdenum glass melting electrodes today in the popular 1¼" diameter size. (Other sizes are available on request.) Choose from random lengths 12 to 75 inches or specified cut lengths up to 72 inches. In ordering, you need only specify the length, plus any special operation such as drilling and tapping.

For more information,

write for Product Data Sheet 2200-a: General Electric Co., Lamp Metals and Components Department GI-012, 21800 Tungsten Road, Cleveland 17, Ohio. (In Canada write: Canadian General Electric Co., Ltd., Component Sales, 221 Dufferin St., Toronto 3, Ontario.)

Progress Is Our Most Important Product

GENERAL ELECTRIC

NEW EQUIPMENT AND SUPPLIES

Polariscope

A bench or portable polariscope used to detect strains in laboratory glassware, tempered glass, glass-to-metal seals, and optical frames. Lens distance can be adjusted for specimens of any diameter. To inspect extremely large pieces, the lens can be removed by turning a wing nut.

Bethlehem Apparatus Co., Hellertown, Pa.

Vibrating Screen Feeder

Separates mixed loads of solid materials, or solids and liquids, and moves them to collection points where they can be deposited in separate containers. Intensity and frequency of vibration can be regulated by adjusting the air supply to the vibratory unit. Units can be floor mounted or suspended.

The Wellman Co., Investment Insurance Bldg., East 6th at Rockwell, Cleveland 14, O.

Zircon Mortar

Designed to bond zircon bricks and shapes in glass melting furnaces, enamel smelting furnaces, and metallurgical furnaces at temperatures up to 3,600°F. Contains no added clays or aluminous materials. Shipped dry in 100 lb. bags.

H. K. Porter Co., Inc., Porter Building, Pittsburgh 19, Pa.

Infra-Red Burner

Designed specifically for low-temperature industrial processing applications including: drying metals, curing shell molds and foundry cores, drying porcelain-enamel frit, drying moist fabrics, and drying of enamel and paint.

Radiant heat emission is concentrated in the 2.0 to 4.0 micron band. Nominal heat input is 30,000 BTU for each 4 x 18-in. burner screen. Face temperature of each burner screen may be regulated up to 1800°F. The cast-iron integral manifolds can be assembled into continuous lines up to 100 ft. long. Manifolds will light end-to-end from a single pilot—from one line to an adjacent line when assembled in solid banks.

Bryant Industrial Products Corp., 17700 Miles Ave., Cleveland 28, O.

Lens Cleaner

A lens cleaning station with two one pint plastic bottles of liquid that clean and anti-fog safety glasses, prescription glasses, face shields, windows and mirrors. Each bottle is equipped with a spray pump for applying liquid to lenses.

Albert W. Pendergast Safety Equipment Co., Tulip and Longshore Sts., Philadelphia 35, Pa.

Bridge Breaker

A bridge breaker for moving hard to handle materials which have a tendency to bridge, cake, or otherwise obstruct continuous flow through bins.

Vibrators mounted on the outside bin walls shake expanded metal screens mounted inside the bin by means of shock mounted studs that pass through the bin walls. The screen's motion is parallel to the sides of the bin therefore material does not tend to compact. Screen sections are adaptable to either flat or conical surfaces and are available for areas up to four square feet, depending on the kind of material and bin configuration.

John S. Blackwell, Thayer Scale Corp., Thayer Park, Pembroke, Mass.

Woven Wire Filters

Wire element-in-line filters in 20 basic types with removal ratings from 1½ microns to 149 microns or coarser. Fluids ranging from cold gases to hot viscous polymers may be handled over the temperature range of 320°F. to plus 1000°F. Housings are constructed of aluminum, stainless steel, Monel and other materials.

Pall Corp., Glen Cove, N. Y.

Motion Safety Switch

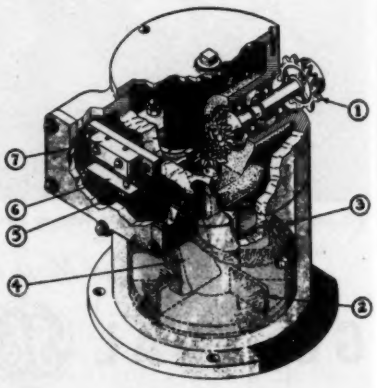
This motion safety switch is designed to protect machines, equipment, and processes against damage resulting from stoppages.

The device is driven by constantly-running machinery or equipment essential to the safe operation of related equipment or processes. The switch's method of operation is illustrated.

1. Drive shaft sprocket. A small chain drive (not shown) connects this drive shaft to the driven shaft of the equipment to be protected.
2. Horizontal paddle wheel.
3. Body of oil.
4. Vane.
5. Half-round, half-flat, horizontal shaft end.
6. Hinged leaf.
7. Micro-switch.

In normal operation the drive shaft, via two bevel gears, turns the paddle wheel in a body of oil. The movement of the oil tilts the vane to which is attached the half-round, half-flat, horizontal shaft end. When the oil movement stops, the vane hangs vertically and the flat portion of the horizontal shaft end appears under the hinged leaf. The leaf drops thus actuating the micro switch to either close or open the circuit as desired.

Fuller Co., Catasauqua, Pa.



Bunker Vibrators

Electromechanical rotary vibrator for use in large bunkers of wood, steel, or concrete.

The vibrator is mounted on a long (up to 50 ft.) strip of steel which is suspended into the bunker directly over its discharge opening. When in operation, the vibrator shakes the steel strip violently and breaks down arching or plugging of the material.

Syntron Co., 156 Lexington Ave., Homer City, Pa.

Laboratory Glass Identification

A full line of laboratory glassware items bearing a positive, permanent symbol from the Atomic Energy Commission reading: "Caution—Radioactive Material." The identification marker reduces radiation hazards existing in make-shift identification methods. It is particularly important in the washing of laboratory glassware where human classification errors are liable to occur.

Fischer & Porter Co., 599 Jacksonville Rd., Warminster, Pa.

Heavy Duty Scale

Portable platform scale with two capacities, 500 lbs. with 8 oz. graduations and 100 lbs. with 1 lb. graduations, can be used for many heavy duty industrial and commercial weighing operations. An adjustable hydraulic damper controls weighing speeds over a wide range.

The cast iron platform is elevated 8¼″ above the floor and measures 18″ x 27″. The over-all height from floor to top of scale is 71½″. Scales are available without wheels for top of floor use or pit mounted installations.

The Exact Weight Scale Co., 541 East Town St., Columbus 15, Ohio.

Filament Mounting

Self-monitoring assembly machine for ignitor filaments used in photoflash lamps and detonators. Assembles 1,200 pieces per hour using two spools of copper-clad wire, a spool of 0.003″ diameter tungsten wire as the ignitor, and preforms of glass.

A monitoring station inspects the finished part for presence or absence of ignitor wire. Rejects are bent out of shape and ejected at inspection station. Machine can be modified to assemble other similar electronic and mechanical components.

Eisler Engineering Co., Inc., Newark 3, N.J.

Lighting Leases

A plan allowing modern lighting equipment to be rented for monthly payments. Installation costs up to 50 per cent of the selling price of the lighting equipment can be included in the leases. Leases are available for periods of two, three, or five years.

Westinghouse Credit Corp., 933 Penn Ave., Pittsburgh 22, Pa.

Inspection Light

Inspection light for visual inspection of empty and filled glass bottles and containers in processing plants. Permits product inspection as to general appearance, color, filling line level, quality. Lights may be mounted on production line conveyor assemblies or divider combiner conveyors. For semi-opaque brown, green or amber colored containers sodium vapor lights are provided.

Terriss-Consolidated Industries, 22 Wooster St., New York 13, N. Y.

Turn Table

Built of welded steel construction with machined hot rolled plate tops. Drive to turn table is connected by means of a standard Boston coupler and speed is variable from 20 to 60 ft. per minute at outer periphery of top plate. Adjustable guide rail is coated to allow minimum frictional contact with product being handled. Nominal height is 30″.

Stone Conveyor Co., Inc., Honeoye, N.Y.

Jackstacker

Equipped with a side shifter and counterbalance which enables load moving to 4″ on either side of center without moving the truck. Standard forks are interchangeable with rams, gooseneck cranes and other mechanical accessories.

Lewis-Shepard Products, Inc., Dept. R10-57, 125 Walnut St., Watertown 72, Mass.

Thermocouple

Refractory metal thermocouple combination for reliable temperature measurement up to 2800°C. for use in vacuum, hydrogen or inert gases such as nitrogen, argon and helium. Combination consists of tungsten 26% rhenium and should not be used under oxidizing conditions or in the presence of hydrocarbon vapors as they will attack tungsten at temperatures above 1000°C.

Engelhard Industries, Inc., 75 Austin St., Newark 2, N.J.

Ultrasonic Cleaning

Ultrasonic cleaning systems designed to provide maximum cleaning power at a constant rate. Activated by fully-transistorized electronic generators. Units compensate automatically for changes in both load and liquid levels. Utilizes a newly-devised semiconductor circuit to eliminate all tuning adjustments and meter readings.

Acoustica Associates, Inc., c/o Wolcott & Associates, Inc., 1308 Wilshire Blvd., Los Angeles 17, Calif.

Temperature Control

Dual switch indicates temperature control for such applications as ovens, baths, environmental test chambers, molding machines, and plant processes.

Up to four independent circuits can be controlled and the two separate switches permit switching action above or below the index set point. Bellows which expand or contract with heating or cooling actuate the switches at preset temperature points.

L. E. Pratt, United Electric-Controls Co., 79 School St., Watertown 72, Mass.

Flow Switch

Designed to either automatically correct lack of material at a critical point in bulk material handling systems or sound an alarm. Shortage of material causes switch to activate an electromagnetic bin vibrator which breaks down arching or plugging in bin, hopper or chute. Switch rating is 1 ampere at 115 volts and .5 ampere at 230 volts, a.c.

Syntron Co., 156 Lexington Ave., Homer City, Pa.

Antimony Oxide

Used in the manufacture of glass, porcelain enamel and pottery. Typical analysis is listed as: Sb_2O_3, 99.645%; SiO_2, 0.055%; PbO, 0.043%; Fe_2O_3, 0.045%; SO_2, 0.146%; As_2O_3, 0.066%.

Samincorp South American Minerals & Merchandise Corp., 425 Park Ave., New York 22, N. Y.

Recording Spectrophotometer

To be used for color measurements in ceramic tiles, textiles, pigments and dyes. The spectrophotometer automatically produces a graph of reflectance versus wavelengths, which becomes a permanent "optical fingerprint" for the file. Colors are described with numbers in precise mathematical form.

General Electric Co., Schenectady 5, N. Y.

INVENTIONS AND INVENTORS

Feeding and Forming

Apparatus for Manufacturing Glass Beads. Patent No. 2,945,326. Filed May 9, 1958. Issued July 19, 1960. Two sheets of drawings; none reproduced. By Thomas K. Wood.

Apparatus is shown for producing glass beads of small diameter comprising a vertically disposed draft tube. Means are provided for introducing a stream of glass particles above the source of heat. An enlarged expansion chamber communicates with the vertical draft tube and permits the blowing of the beads. A collecting chamber is provided at the bottom of the expansion chamber.

The patent contains many controls and improvements in bead recovery to make the process more economical than previously employed manufacturing methods.

There were 3 claims and the following references cited in this patent.

United States Patents

2,306,462, Moorman, Dec. 29, 1942; 2,334,578, Potters, Nov. 16, 1943; 2,421,902, Neuschotz, June 10, 1947; 2,619,776, Potters, Dec. 2, 1952; 2,838,881, Plumat, June 17, 1958.

Furnaces

Recirculating Furnace. Patent No. 2,945,325. Filed May 7, 1957. Issued July 19, 1960. Five sheets of drawings; none reproduced. Assigned to Knox Glass, Inc., by William B. Deible and Harold A. Youkers.

This invention relates generally to the conditioning of molten material in a furnace preliminary to forming or shaping it at an elevated temperature. It deals with the problem of providing better heat utilization and better control of the runout in a furnace in preparing and delivering a suitable material, such as a vitreous or plastic material, so that it may be formed or shaped into suitable articles.

The invention deals with means for moving or returning a portion of the hot molten or fluid materials from one chamber back to another chamber of the furnace to provide an improved and novel type of convection flow of the material, wherein only a portion, for example a third, of the outflow from one chamber into another may continue on for delivery or pull-out, while the other or major portion, for example, two thirds; may be returned to the conditioning or melting chamber; relative rate or speed of flow is the level-maintaining factor. Any suitable multiple arrangement employing such a principle may be utilized, depending upon the requirements as to draw-out, quality of the material, etc.

There were 2 claims and the following references cited in this patent.

United States Patents

1,812,975, Morton, July 7, 1931; 1,916,668, Howard, July 4, 1933; 1,959,417, Flexon, May 22, 1934; 1,973,689, Geer, Sept. 11, 1934; 1,999,762, Howard, Apr. 30, 1935; 2,189,271, Rowe, Feb. 6, 1940.

Glass and Wool Fiber

Apparatus for gaseous metal plating fibers. Patent No. 2,887,088. Filed August 14, 1954. Issued May 19, 1959. No sheets of drawings; none reproduced. Assigned to The Comonwealth Engineering Company of Ohio by Herman R. Nack.

It is a particular object of the present invention to provide a novel method for the metalizing fibers, by providing a swirling atmosphere of a heat decomposable metal bearing compound and passing the heated strand of the material longitudinally through the swirling atmosphere at a relatively high rate of speed to insure adequate decomposition of the gas and the metalization of the filament.

Glass fiber rovings are drawn through an apparatus and attained at the heating rolls a temperature of between about 450-475°F prior to entry to the plating chamber. The plating chamber through the outer stationary elongated housing is supplied with the swirling atmosphere of nickel carbonyl gas. The rate of gas flow through the housing is about 4 liters per minute at a temperature of about 78°F, the pressure internally of the chamber being only very slightly less than that of atmospheric.

The fiber was drawn longitudinally through this chamber at a rate of about 75 feet per minute and the chamber in this instance was suitable for such a length as to expose the fiber to the gas for approximately 4 seconds. Thereafter the metal treated fiber was wound and allowed to cool in the atmosphere.

The nickel deposit under these conditions is sufficient to provide the glass fiber rovings with a conductivity of approximately 2500 ohms per inch and each of the filaments of the roving, which are approximately 1600-2000 in number, are uniformly coated.

An important object of the invention is to provide apparatus in which a swirling atmosphere of a gaseous decomposable metal bearing compound is provided by high speed rotation of a tubular body containing the atmosphere.

There were two claims and seventeen references cited in this patent.

CURRENT STATISTICAL POSITION OF GLASS

Employment in the glass industry during August, 1960, was as follows: *Flat Glass*: a preliminary figure of 25,400 for August, 1960, indicates a decrease of 1.5 per cent under the adjusted figure of 25,800 reported for July, 1960. *Glass and Glassware, Pressed and Blown*: an increase of 0.7 per cent is shown by the preliminary figure of 90,700 reported for August, 1960, when compared with the adjusted figure of 90,000 reported for July, 1960. *Glass Products Made of Purchased Glass*: the preliminary figure of 13,800 given for August, 1960, is 2.9 per cent over the adjusted figure of 13,400 reported for July, 1960.

GLASS CONTAINER SHIPMENTS
(All Figures in Gross)

Narrow Neck Containers

	September, 1960
Food	2,729,000
Medicinal and Health Supplies	1,327,000
Chemical, Household and Industrial	934,000
Toiletries and Cosmetics	865,000
Beverage, Returnable	483,000
Beverage, Non-returnable	127,000
Beer, Returnable	70,000
Beer, Non-returnable	890,000
Liquor	904,000
Wine	401,000
Sub-total (Narrow)	8,730,000

Wide Mouth Containers

Food	*4,313,000
Medicinal and Health Supplies	394,000
Chemical, Household and Industrial	159,000
Toiletries and Cosmetics	208,000
Dairy Products	210,000
Sub-total (Wide)	*5,284,000
Total Domestic	14,014,000
Export Shipments	*156,000
TOTAL SHIPMENTS	*14,170,000

* This figure includes Fruit Jars, Jelly Glasses, and Packers' Tumblers.

GLASS CONTAINER PRODUCTION AND INVENTORY
(All Figures in Gross)

		Production September 1960	Stocks September 1960
Food, Medicinal and Health Supplies; Chemical, Household and Industrial; Toiletries and Cosmetics	Narrow Neck	5,100,000	6,792,000
	Wide Mouth	*4,598,000	*6,607,000
Beverage, Returnable		462,000	2,245,000
Beverage, Non-returnable		102,000	304,000
Beer, Returnable		82,000	467,000
Beer, Non-returnable		1,007,000	847,000
Liquor		1,013,000	1,642,000
Wine		365,000	703,000
Dairy Products		170,000	300,000
TOTAL		*12,899,000	*19,907,000

* This figure includes Fruit Jars, Jelly Glasses, and Packers' Tumblers.

Payrolls in the glass industry during August, 1960, were as follows: *Flat Glass*: a decrease of 4.2 per cent is shown in the preliminary $13,297,231.72 given for August, 1960, when compared with July's $13,891,199.36. *Glass and Glassware, Pressed and Blown*: an increase of 2.4 per cent is shown in the preliminary $36,584,658.58 given for August, 1960, when compared with the previous month's adjusted $35,697,853.80. *Glass Products Made of Purchased Glass*: a preliminary figure of $4,468,388.92 was reported for August, 1960. This is an increase of 2.8 per cent when compared with the adjusted figure of $4,345,375.05 for July, 1960.

Glass Container Production based on figures released by the Bureau of the Census, Industry Division, was 12,899,000 gross during September, 1960. This is a decrease of 17.6 per cent under the previous month's production figure, 15,671,000 gross. During September, 1959, glass container production was 11,872,000 gross, or 7.9 per cent under the September, 1960 figure. At the end of the first nine months of 1960, glass container manufacturers have produced a preliminary total of 123,362,000 gross. This is 5.5 per cent more than the 116,929,000 gross produced during the same period in 1959.

Glass Container Shipments during September, 1960, came to 14,170,000 gross, a decrease of 13.1 per cent under August, 1960, which totaled 16,312,000 gross. Shipments during September, 1959, amounted to 12,546,000 gross, or 11.5 per cent under September, 1960. At the end of the first nine months of 1960, shipments have reached a preliminary total of 120,245,000 gross, which is 0.005 per cent less than the 120,252,000 gross shipped during the same period of the previous year.

Stocks on hand at the end of September, 1960, came to 19,907,000 gross. This is 7.4 per cent under the 21,500,000 gross on hand at the end of August, 1960, and 55.7 per cent more than the 12,785,000 gross on hand at the end of September, 1959.

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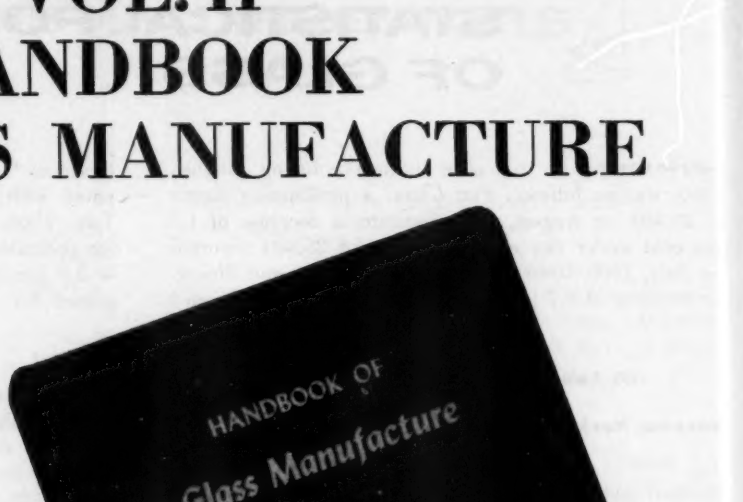

Volume II of the Handbook of Glass Manufacture deals with a number of significant and important topics in the glass industry, some of which augment the subject matter in Volume I, others extend it.

The basic purpose and philosophy of Volume I has been preserved in Volume II and, again, a major concept is to bridge the gap between theory and practice . . . and to provide for the production executive, the engineer, technologist and scientist an effective starting point for approaching many of the practical problems which confront him in the course of his work.

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FALL GLASS DIVISION MEETING

(*Continued from page* 683)

slabs have same thermal properties, *(b)* slabs have different thermal properties, and *(c)* there is contact resistance between slabs. Also considered was the two-dimensional example where one of the slabs prossessed a corner. The significance of these calculations to glass forming was briefly discussed.

Preparation of Oxide Glass Films by Reactive Sputtering

By *W. Robert Sinclair* and *F. G. Peters*, Bell Telephone Laboratories, Inc., Murray Hill, N. J. Presented by Mr. Sinclair.

A method for depositing oxide glass films on a substrate was presented. The method involved the sputtering of a metal electrode in a reactive atmosphere (reactive sputtering). The films obtained were of good quality, unstrained, and adhered well to the substrate. There was no apparent limiting thickness for the process, and the substrate did not need to be heated during the process. The preparation of lead tellurite glass films, silica glass films, and silicate glass films was described.

It was shown that with reactive sputtering techniques glass films can be prepared of a variety of different oxide systems by use of the appropriate pure metal or alloy as the cathode. These films have been deposited successfully on many different types of inorganic substrates and adhere well. (*To be concluded next month*)

CONDITIONS OF GLASS FORMATION

(*Continued from page* 695)

which one or more O^{2-} ions are replaced by F^- ions. Therefore, cations of this type may lower the opacity of a fluoride opal glass and help to make fluorides and silicates more compatible. This feature is used in optical glasses for retaining a major concentration of fluorine.

Boron, too, acts in the same way. The B^{3+} core is well screened by three anions as can be seen from the fact that BF_3 is a gas. The B^{3+} core can easily expand its coordination to four as can be seen from the existence of the fluoroborates, e.g., KBF_4. Hence the presence of B_2O_3 in a silicate glass increases the compatibility of the glass with fluorides in a way which makes borosilicate glasses unsuitable for opacification with NaF.

No such aversion exists between the Si^{4+} ions and the better screening Cl^-, Br^- or S^{2-} ions. Chloride and sulfide ions are better screeners than F^- ions so that $SiCl_4$ and SiS_2 are formed more readily in a glass melt than SiF_4. Indeed, it is not possible to retain a major concentration of chloride and sulfide ions in a soda lime silicate glass because of the formation of volatile compounds. Compatibility of such a glass with sulfides can be achieved by introducing into the glass a cation such as Zn^{2+} or Cd^{2+} which due to its stronger polarizing power (eighteen shell) surrounds itself preferentially with the more polarizable S^{2-} ions. The retention for sulfur and selenium by a silicate glass is approximately proportional to its zinc oxide content. In this case it is the greater mutual deformation between a non-noble gas type cation and the more polarizable S^{2-} and Se^{2-} ions which modifies the place changes between anions in the glass melt and keeps the number of S^{2-} ions surrounding a Si^{4+} ion to a minimum.

The Cl^-, Br^-, and I^- ions escape readily from a silicate or a borosilicate glass because of the volatility of the halides of silicon and boron. Like the S^{2-} ions, the I^- ions can be retained by cations of the transition elements. Green borosilicate glasses have been made which contain $(Co^{2+}I_4^-)^{2-}$ groups[23].

RADIANT HEATING

(*Continued from page* 686)

"stop" board on the conveyor belt to show how unsatisfactory glass pieces are carried to a metal "reject" chute. This connects with a conveyor under the floor that removes broken parts, trimmings or waste glass, and rejects from the building.

After annealing and inspection, the vials, and those ampules which require no printing are packaged for shipment. Ampules that require printing are taken to a

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Sworn to and subscribed before me this 27th day of September, 1960.

Leonard Bhaerman
No. 41-5310850
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46-foot lehr at the end of the annealing line. Here an operator removes the cardboard and corrugated strips from the ampule box and empties the ampules into feeder. This unit automatically introduces the ampules into a screener, where the label is applied onto each glass surface by silk screen printing. The ampules are automatically dropped onto conveyor fixtures and carried into the lehr where printing is fused into the glass.

The heating section at the front of this lehr is 26 feet long. Radiant burners are strategically patterned along both sides of the lehr and individually controlled (Fig. 7). The burners are adjusted precisely for a gradual increase of temperature up to a peak slightly over 1200°F at the mid-point of the heating zone. There is a gradual decrease of temperature towards the end of the heating zone. Temperatures are accurately controlled by a special instrument panel board (Fig. 7) which takes care of all steps throughout the entire operation.

Close control of the temperature curve in this lehr is equally as important as it is in the annealing lehrs, if not more so. The correctly annealed qualities and the shape of the ampules must be maintained. In addition, temperatures must be brought precisely to predetermined levels and controlled to within ± 5°F, or the silk screen printing will not properly fuse into the glass.

Quick passage through the controlled heating zone (approximately 1½ minutes) brings the ampules accurately to 1180°F, the temperature required for effective fusing of silk screen printing into the type of glass used. After another 1½ minutes in the controlled cooling zone, 3 minutes total time in the lehr, the ampules emerge (Fig. 8) and are inspected by an operator for clean, clear, unsmeared printing. They are then packaged for the rigid quality control tests which follow.

The flame-burner method used previously proved even more costly in this operation than it had in the annealing lehrs, because of the company's strict quality and reject policies and its ruling against re-runs, and because at this point in the operation all work has been completed on the pieces.

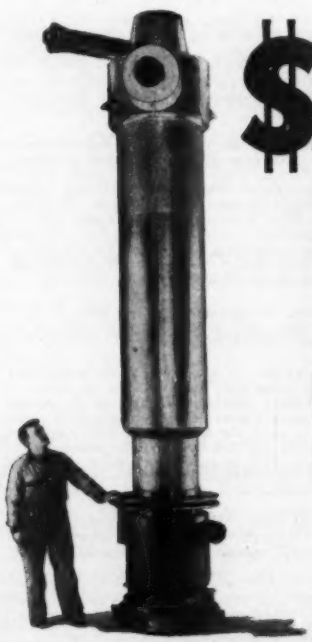
Radiant heating has eliminated printed ampule rejects, and at the same time, it has doubled the production speed of this process.

Conclusion

These heating methods have more than doubled conveyor belt life in the 19 annealing lehrs. Belts used to be replaced after six months. In the little over one year that the radiant heated lehrs have been operating, not one conveyor belt has shown the slightest need for replacement.

Not a single lehr has been down for repairs, despite the heavy 18- and 24-hour plant operating schedules.

Another advantage, and a big fuel-saver, is speed of heatups. Each lehr requires only 12 to 15 minutes to reach 1200° from room temperature.



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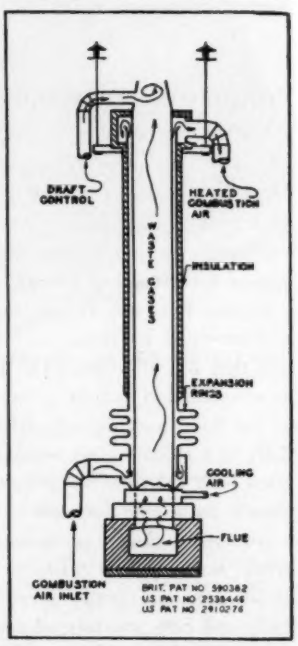

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HIGH MODULUS GLASS FIBERS

(*Continued from page* 700)

to find an operable high modulus glass. This work[3] was carried out under the sponsorship of WADD.

Viscosity and liquidus determinations, and estimated devitrification rates were obtained for each of these glasses. For the most part, the glasses had high liquidi or unfavorable viscosity-temperature relationships, and were soon eliminated. Those that appeared likely to be operable were tested in a one-hole bushing. Moduli were measured on fibers produced. Note should be made here of the fact that values reported for the modulus of a given glass are dependent upon its thermal history. Maximum values are found for fully annealed glass. Fibers as drawn are usually found in a state as far removed from perfectly annealed glass as one is likely to encounter. Consequently, modulus measurements made on fibers are lower than those obtained on annealed bulk glass of the same composition. This difference usually amounts to between one and two million psi, but variations as high as four million have been reported. Modulus measurements made on fibers are to be preferred over those made on bulk glass, where application in reinforced plastics is being considered, although measurements are often made on bulk glass samples for convenience. Heat treatments of fibers tend to cause their modulus to approach that of bulk glass.

Properties of YM-31-A

Of the sixty-two compositions tested, one designated as YM-31-A appeared to offer the best compromise between glass properties and forming difficulty. The chemical composition of this glass is given in Table 1.

Table 1: Glass Compositions

YM-31-A		"E" Glass	
Component	Per Cent	Component	Per Cent
SiO_2	53.7	SiO_2	54.5
CaO	12.9	Al_2O_3	14.5
MgO	9.0	CaO	17.0
BeO	8.0	MgO	4.5
ZrO_2	2.0	B_2O_3	8.5
TiO_2	8.0	Na_2O	1.0
Li_2O	3.0	K_2O	
CeO_2	3.0	TiO_2	
Fe_2O_3	0.5	Fe_2O_3	

The composition of "E" glass is given for comparison. YM-31-A has a modulus in fiber form of approximately 16 million psi, which is approximately 50 per cent higher than that of "E" glass. The liquidus is of the same order as "E" glass. The viscosity is somewhat low, making the viscosity at the liquidus near the critical value, but the relationship appeared to be as favorable as any found for glasses with modulus of this magnitude.

The durability of glass is a difficult property to evaluate. This is true because, in general, the resistance of glass to chemical attack is high. If conditions severe enough to cause a measureable attack in a reasonable length of time are imposed upon the glass, then inter-

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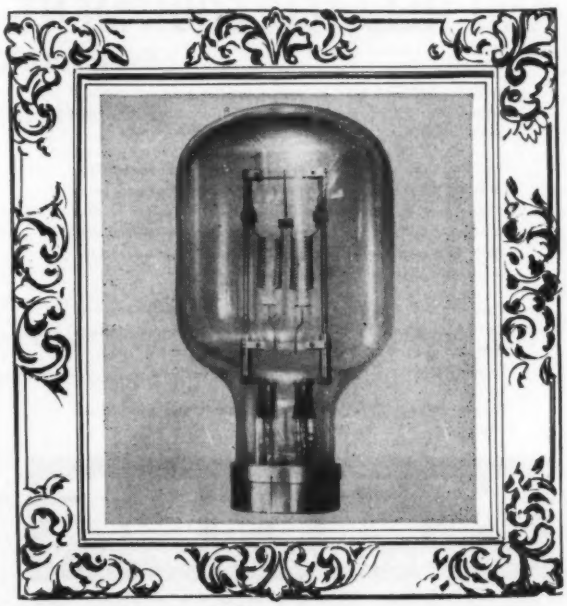

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preting the results so as to predict what would happen under normal conditions is quite uncertain. A standard test[4] run on crushed glass indicates that YM-31-A offers excellent resistance to chemical attack by water and fair resistance to acid attack. The density of YM-31-A is somewhat higher than that of "E" glass, 2.89 grams per cubic centimeter vs. 2.58 for "E" glass.

Figure 1 shows the tensile strength of bare single fibers of YM-31-A as a function of temperature. It will be noted that these fibers have the same high strength as possessed by "E" glass at room temperature. As might be expected from the lower viscosity, the strength drops off somewhat more rapidly for YM-31-A than for "E" glass at elevated temperatures, but not seriously so.

Figure 2 shows the change in modulus as a function of temperature for YM-31-A and for "E" glass fibers. Note that these fibers have been heated to 930°F prior to testing, and that the modulus values are higher at the beginning than would normally be expected. The modulus tends to drop off in both cases as the temperature is raised. The modulus of YM-31-A remains well above that of "E" glass in all cases. The highest modulus measurement obtained on YM-31-A, 17.4 million, is not indicated on the graph. It was obtained after heating a fiber for two hours at 1150°F.

Preparation of YM-31-A in a Multi-hole Bushing

Predictions made on the basis of laboratory data were entirely borne out when attempts were made to produce YM-31-A glass in a multi-hole bushing at a rate approaching commercial practice. As predicted from the viscosity-liquidus relationship, the fiber forming operation of this glass is quite critical. A special bushing had to be used in which there were no relatively colder spots in which devitrification could occur. Exceptionally good control of process variables, such as temperature and glass head, was required and was obtained. Only cullet of the highest quality was acceptable. As a point of interest, it was found that glass defects of a type which would never be noticed when using bulk glass for optical purposes were sometimes present, and when they were, they caused the glass to be completely unusable in the continuous fiber forming operation.

The fibers had the properties expected of them. Modulus measurements varied between 15.85 and 16.0 million psi. Tensile strength of the yarn was satisfactory. No durability problem or deterioration in storage was found. Samples adequate for evaluation in plastic laminates were made. The results of this evaluation are to be reported later.

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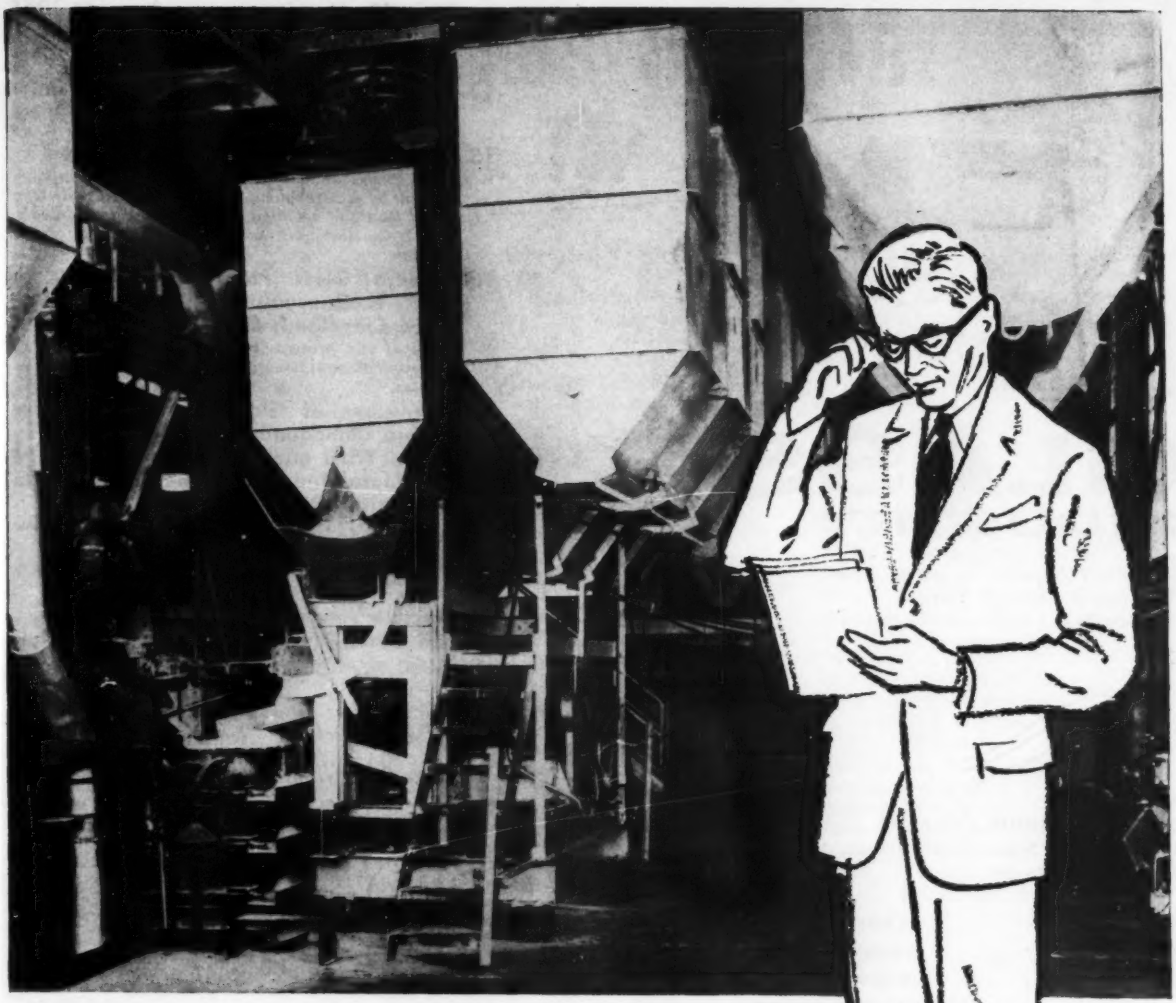

Furnace charging floor showing mixed batch storage and handling.

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